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A Literature Review

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Representative studies of the environmental significance of inorganic species (as opposed to total-element content) in water are reviewed. The effects of chemical forms on human health and on plant and animal life, and the roles of valence state, ionization, complexation, and adsorption in the transport and cycling of elements are considered along with factors affecting the distribution of elements and species in freshwater streams and impoundments, in estuaries, and in the sea.

Information on the chronic effects on human health of trace inorganic pollutants in water is almost entirely limited to total elements because of an inability to distinguish among forms of an element. The elements of greatest concern with respect to the toxicity of different species are arsenic, chromium, lead, mercury, and selenium. In the toxicology of aquatic biota, there is a rapidly growing appreciation that both acute and chronic effects are strongly related to chemical species.

The movement of inorganic pollutants in the aquatic environment is strongly influenced by adsorption of particular species on both mineral and organic particulates.

No broadly applicable analytical techniques of adequate sensitivity are available for elemental speciation. This deficiency in analytical ability prevents the evaluation of research on toxicology and on transport of these chemical forms.

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INORGANIC SPECIES IN WATER:
ECOLOGICAL SIGNIFICANCE AND ANALYTICAL NEEDS
(A Literature Review)

by

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FOREWORD

Nearly every phase of environmental protection depends on a capability to identify and measure chemical pollutants in the environment. The Analytical Chemistry Branch of the Athens Environmental Research Laboratory develops techniques for identifying and measuring chemical pollutants in water and soil.

This report summarizes recent literature on the ecological significance of chemical forms of elements, as opposed to total elemental composition, in the aquatic environment. It includes research into the toxicology, transport, transformation, and distribution of inorganic species and the analytical methods that have been used for their determination. This report will acquaint researchers and administrators with the current application of knowledge about speciation and with the needs for improved analytical techniques.

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Director
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ABSTRACT

Representative studies of the environmental significance of inorganic species (as opposed to total element content) in water are reviewed with particular emphasis on the effects of chemical forms on human health and on plant and animal life. Primary attention is given to recent U.S. Government reports and conference proceedings. The roles of valence state, ionization, complexation, and adsorption in the transport and cycling of elements are considered along with factors affecting the distribution of elements and species in freshwater streams and impoundments, in estuaries, and in the sea.

Information on the chronic effects on human health of trace inorganic pollutants in water is almost entirely limited to total elements because of an inability to distinguish among forms on an element. The elements of greatest concern with respect to the toxicity of different species, however, are arsenic, chromium, lead, mercury, and selenium. In the toxicology of aquatic biota, there is a rapidly growing appreciation that both acute and chronic effects are strongly related to chemical species.

The movement of inorganic species in the aquatic environment is strongly influenced by adsorption on both mineral and organic particulates. Adsorption is highly dependent on the chemical species of the pollutant.

No broadly applicable analytical techniques of adequate sensitivity are available for elemental speciation. This deficiency in analytical ability prevents the evaluation of research on toxicology and on transport of these chemical forms.

CONTENTS

Foreword iii
Abstract iv
Acknowledgments vii
1. Introduction 1
2. Conclusions 3
3. Recommendations 4
4. Biological Effects 5
   Enzyme Systems 5
   Bacteria and Phytoplankton 6
   Algae 7
   Daphnids and Molluscs 9
   Fish 10
   Mammals 17
   Interactions of Toxicants 18
5. Human Health Effects 21
   Acute Versus Chronic Effects 21
   Cardiovascular Disease 22
   Elements of Concern 22
6. Environmental Transport and Transformations 28
   Interaction of Water and Solids 28
   Biogeochemical Cycling 33
   Distribution of Elements and Species 36
7. Analytical Methodology 40
   Equilibrium Calculations 41
   Direct Species Determination 42
   Separation Techniques 48
8. References 51

LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

AAS -- atomic absorption spectroscopy
AF -- application factor
ALA-D -- delta-aminolevulinic acid dehydratase
ASV -- anodic stripping voltammetry
DPP -- differential pulse polarography
EDTA -- ethylene diamine tetraacetic acid
GOT -- glutamic oxalacetic transaminase
ISE -- ion-selective electrode
LC_{50}-96 hr -- lethal concentration (to 50% of population in 96-hour exposure)
LSV -- linear sweep voltammetry
MATC -- maximum allowable toxic concentration
NTA -- nitrilotriacetic acid

SYMBOLS

Ag -- silver
Al -- aluminum
As -- arsenic
B -- boron
Ba -- barium
Ca -- calcium
Cd -- cadmium
Co -- cobalt
Cu -- copper
Cr -- chromium
dL -- deciliter
Fe -- iron
Hg -- mercury
K -- potassium
L -- liter
Mg -- magnesium
Mn -- manganese
µg -- microgram
µm -- micrometer
Mo -- molybdenum
Na -- sodium
ng -- nanogram
NH_4^+ -- ammonium
Ni -- nickel
P -- phosphorus
Pb -- lead
pH -- hydrogen ion activity
ppb -- part per billion
ppm -- part per million
Ru -- ruthenium
S -- sulfur
Se -- selenium
Sn -- tin
Tl -- thallium
Zn -- zinc

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SECTION 1

INTRODUCTION

Despite a growing recognition that the chemical forms of elements in the aqueous environment have a critical effect on the toxicity of pollutants to aquatic biota and on the transport and recycling of inorganic pollutants, regulatory standards necessarily are based largely on total-element concentrations because of a lack of adequate analytical methodology for individual species. This deficiency in analytical ability is probably even more serious in the evaluation of research on toxicology and on transport, and in the evaluation of models in either of those areas.

The toxicology, distribution, and analytical chemistry of heavy metals in the aquatic environment was the subject of an international symposium (270), and the relation of speciation to aquatic toxicology was considered in another symposium (15), but the broader ecological aspects of inorganic speciation have not been summarized.

This literature review is intended to provide researchers and administrators with a coordinated assessment of the significance of inorganic speciation in natural waters and, secondarily, to provide direction for a program to develop elemental analytical methodology to meet EPA's research and standards-setting needs.

Excluded from this review are organic species except as complexants for metal ions. The nutrient species of phosphorus are included only as they interact with other inorganic forms. Only a very small sampling of the literature on radionuclides has been included.

The review is far from comprehensive. Few secondary references have been obtained and many sources have been examined only in abstract form. In all such cases, the source of the abstract is indicated in the bibliography. Particular emphasis was given to coverage of U.S. Government reports, which might be less readily available than formal scientific journals. To this end, three computer searches of technical information files were utilized. The author accepts responsibility for any deficiencies in coverage but believes that a broad enough sampling has been obtained to meet his objectives.

A conscious effort was made to limit the coverage to references dealing specifically with chemical species, as opposed to total element concentrations. The operational definition of a species, however, depends upon the analytical method used to determine it. In many cases the dominant, stable form (free ion for example) was assumed even when a total-element analysis was used.

SECTION 2

CONCLUSIONS

Information on the chronic effects of trace inorganic pollutants in water on human health is almost entirely limited to total elements because of an inability to distinguish among forms of an element. Speciation affects the distribution and availability of elements in water supplies, and toxic synergism or antagonism among elements suggests chemical interactions dependent on species.

In the toxicology of aquatic biota, especially fish, there is a rapidly growing appreciation that both acute and chronic effects are strongly related to the chemical species of the toxicant. For heavy metals, it appears in most cases that the free atomic ion is the only, or most, toxic form.

The transport, transformation, and distribution of inorganic pollutants in the aquatic environment is strongly influenced by adsorption on both mineral and organic particulates. Adsorption, which may be either physical or chemical in nature, is highly dependent on the chemical species of the pollutant.

Although many fewer inorganic species, than organic, are significant in water, the inorganic forms are not biodegradable and some, if not all, seem subject to perpetual cycles of transformation that require constant surveillance from the public health point of view.

No broadly applicable analytical techniques of adequate sensitivity are available for elemental speciation. Consequently, in most studies of the effects of speciation, the inorganic species have been defined operationally by the methods at hand for their determination.

The elements of greatest concern with respect to known or suspected toxicity are different species of arsenic, chromium, lead, mercury, and selenium.

SECTION 3

RECOMMENDATIONS

The chemical species involved, and its effects, should be identified so far as practicable in toxicological and epidemiological studies. The interactions of toxic pollutants, both organic and inorganic, require more study.

Improved analytical methods are needed for surface species on sediment particles. Such a capability would aid both equilibrium and kinetic studies of adsorption.

New and more sensitive ion selective electrodes should be developed. Most crystal-membrane electrodes have practical detection limits much greater than those dictated by the solubility of the crystal but the reasons for the difference are not clear.

The analytical applications of ion exchange should be extended in two areas:

- Concentration of ionic species, especially as a means of extending the detection limits of ion-selective electrodes, and
- Chromatography of ions as a means of separating and identifying several species in a sample.

SECTION 4

BIOLOGICAL EFFECTS

The effects of trace elements, both as the total element and its specific chemical forms, can be studied systematically using plants and lower animals as experimental subjects. It is hoped that the information thus obtained can be extrapolated to the corresponding effects on human health although such attempts must be made with great caution. This Section deals with the effects of chemical species on biota, starting at the subcellular level and advancing into broad classes of plants and animals in order of increasing complexity. Annual reviews in the Journal of the Water Pollution Control Federation (288) provide comprehensive and up-to-date literature surveys of the effects of trace elements on aquatic biota, although material relating specifically to speciation forms only a minor part. The Leland et al. review is particularly noteworthy for a summary on bioaccumulation of trace elements.

ENZYME SYSTEMS

The toxicity of inorganic pollutants is closely related to their effects on essential enzyme systems. A toxic metal ion may replace the essential metal characteristic of a particular enzyme and act, as Schroeder put it (413), "like a key that fits a lock but does not turn." Elements that act this way are usually heavier than the replaced element and in the same, or neighboring, groups of the Periodic Table. Alternatively, the toxic element may form tight bonds with the normally labile linkages of protein ligands. The availability of ions to act in either of these ways may be mediated by non-biological or foreign ligands that form insoluble or stable complexes. If such ligands tie up essential ions, they may lead to deficiency diseases or, if they tie up toxic ions, they may have a protective or antidotal effect. The effects of pollutants on enzymes, analytical applications of enzymes, and biological indicators of pollution have been covered in two bibliographies (208,482). A broader coverage of the biological effects of metals in aquatic environments is provided by the bibliographies of Eisler and Wapner (148,149).

The toxicity of a series of metal ions to aquatic organisms (425) and the inhibition of urease by metal ions (232,427) have both been correlated inversely with the solubility of the metal sulfides, suggesting that binding to protein sulfhydryl groups is the mode of biological action of the metals. The morphology of fish blood cells was altered by Cd and Cu in the water and this effect was proposed as a biological assay technique (117). The effects of Pb(II), Cu(II), Hg(II), Zn(II), and Cd(II) on isolated cell mitochondria have been summarized (67). The extreme toxicity of Cu(II) to mitochondria suggests that living organisms have a protective mechanism that restricts access of Cu inside the cell, but that the mechanism is less effective toward the other heavy metals.

Studies with rat brain tissue indicated that the specific toxic effects of Pb and alkyl derivatives of Hg and Sn could not be defined in terms of a single enzyme, any one subcellular compartment such as the mitochondrion, or even one function of the tissue, but depended on the metabolic organization of the whole tissue (84). Allantoinase was inhibited by 10^{-6} *M* divalent cations of Hg, Cu, Zn, Pb, and Cd, but its activity was enhanced (10-20%) by 2.5 x 10^{-8} *M* concentrations of the same ions (73).

BACTERIA AND PHYTOPLANKTON

The toxicity of heavy metals to bacteria has practical significance in the biological treatment of sewage. Bench tests showed that Cd(II), Cu(II), Ni(II), Zn(II), and Cr(VI) inhibited the digestion of raw domestic sewage; addition of these ions to the influent to an oxidation pond at concentrations up to 6 ppm had no deleterious effect, however, presumably because most of the metals were precipitated by the moderate alkalinity (pH 8) (336). A systematic study of the effects of Na^+, NH_4^+, K^+, Ca^{2+}, and Mg^{2+} ions in anaerobic waste treatment revealed both antagonistic and synergistic interations although most of these ions were tolerated at concentrations less than 0.1 *M* (273). The chelating agent ethylenediamine tetraacetic acid (EDTA) was reported to reduce the toxicity of Cu(II), Hg(II), Ni(II), Cd(II), Zn(II), and Pb(II) in the activated sludge process but was not effective with Ag(I), Co(II), Cr(III), or Cr(VI) (402). At low total concentrations of Ca, EDTA inhibited the growth of ammonia-oxidizing bacteria in activated sludge, although the complexant reduced the toxicity of Cu (298). The self-purification of river water polluted with sewage was inhibited by 0.1 ppm Cu(II) or 1 ppm Pb(II) (251).

Bacteria that were relatively resistant to Hg compounds were isolated from Chesapeake Bay sediment and were able to metabolize $HgCl_2$ or phenylmercuric acetate to elemental Hg (109). Zinc, at 50 ppb, was somewhat more toxic than 10 ppb Cu(II) to a natural population of heterotrophic bacteria (6) and the effects of the combined metals were additive. In the same study, an excess of L-cysteine did not protect the bacteria from the toxic effects of 100 ppb Hg(II) nor did albumin protect from 0.05 ppm Ag(I).

A hydrocarbon-oxidizing yeast, *Rhodoturula rubra*, that has very low phosphate requirements, was studied (86). Under phosphate-limited conditions, arsenate at 10^{-7} to 10^{-8} $\underline{M}$ was taken up competitively with phosphate, and Cu(II) was toxic at 10^{-6} $\underline{M}$. Excess phosphate or trace amounts of Mn(II) protected against the effects of Cu and the authors concluded that Mn impurity in the phosphate was the effective agent. Iron is an essential nutrient that may be limiting in marine or fresh water environments. Marine phytoplankton may require soluble organo-complexes of Fe for chlorophyll production (125), and EDTA has been used to make Fe nutritionally available to algae in autoclaved seawater (290). The addition of either Fe or nitrilotriacetic acid (NTA) temporarily increased phytoplankton photosynthesis in a mesotrophic lake but impeded the process in a eutrophic lake (80). Presumably the additives by precipitation-adsorption of the Fe or chelation of the NTA, removed soluble metals ions from a toxic to nutritional level in the mesotrophic lake, or to a deficiency level in the eutrophic lake.

ALGAE

The major concern has been to find chemicals that can control undesired algal blooms without harmful effects on other aquatic life. Algae have been a convenient form of plant life for investigating toxic effects of metal ions (368).

Copper

Copper is a widely used and effective agent for controlling algal blooms in fresh water. Laboratory studies using cupric ion-selective electrodes have shown that it is the free Cu(II) that is effective (445). Trace amounts are essential and concentrations below 40 ppb were limiting, whereas free Cu(II) concentrations greater than 300 ppb were toxic. In these studies, the availability of Cu was regulated by complexation with EDTA, which had to be used in amounts insufficient to complex all Mg(II). Thus, a competition between Cu(II) and Mg(II) may be involved in the physiological action of Cu in algae. Calcium also reduced the toxicity of Cu to phytoplankton and algae (465). In natural waters, the availability of Cu may be regulated by organic complexants naturally present (335,465) or introduced with sewage effluent (38). During normal growth the blue-green alga, *Anabaena cyclindrica*, produced an extracellular polypeptide that complexed Cu(II), Zn(II), Fe(III), and phosphate. This may be a natural protective mechanism of the plant against Cu (172). In a highly eutrophic lake, the addition of 1/200th the amount of Cu usually used for control inhibited nitrogen fixation by blue-green algae. It was concluded that the natural chelation capacity of the lake was already saturated by indigenous Cu (227). Free Cu(II) at the usual concentration of total Cu in seawater is very toxic to algae; therefore, much of the natural Cu must be complexed (347). The same authors report that ocean upwelling is toxic until chelators are added, indicating that free Cu(II) is more abundant in deep waters.

Silver

Mixtures of Ag and Cu ions were investigated for algal control (508). The combinations were more toxic to one species than the equivalent concentration of Cu, but were less toxic to another algal species. Silver was also more toxic to fish. At 0.15 ppm in Mediterranean seawater, Ag(I) was much more toxic than a similar concentration of either Cu(II), Zn(II), or Hg(II) and appeared to act synergistically with Cu(II) (454).

Mercury

The effect of heavy metal ions on photosynthetic production of oxygen by Chlamydomonas reinhardii leads to the following decreasing order of toxicity: methylmercuric ion > Pb(II), Cd(II) > Cu(II), Hg(II), Tl(I) ≥ Ba(II) (no effect) (360). Both $HgCl_2$ and CH_3HgCl inhibited the biosynthesis of lipids in fresh water algae (317). In a study of algal growth rates, $HgCl_2$ was more toxic than $(CH_3)_2Hg$ (201). Chelation with EDTA reduced the toxicity of both Cu and Hg, but the addition of enough EDTA to complex all the mercury depleted the medium of essential trace nutrients (448).

Selenium

Studies with two species of blue-green algae showed appreciable species difference, but selenite was more toxic to both than selenate (274). This conclusion with respect to blue-green algae was supported in another study (368) that found, in addition, that the growth of diatoms and single-celled algae was stimulated by 1 to 10 ppm selenite. Up to 40 ppm of selenite was tolerated, but all concentrations of selenate were toxic to the single-celled species. Selenium (form not specified) reversed the inhibition of Hg to the growth of Phaeodactylum tricornutum (202).

Lead

Fixation of carbon dioxide by marine algae was reduced 50% in three species by adding 15 to 18 ppm of Pb; however, 5 ppm Pb caused 50% reduction in one species that had a high surface-to-volume ratio (307). The concentrations refer to added Pb, not necessarily to the free Pb(II) in the medium. Another study (506) found that 10 ppm Pb(II) stopped photosynthesis after 24 hours and that 0.1 ppm reduced photosynthesis and respiration by 25 to 50% after 2 to 3 days. Apparently, the Pb penetrated the organisms slowly.

Other Metals

Patrick et al. (368) studied the effects of chemical forms of trace metals on many algal species with the aim of promoting the growth of diatoms and single-celled algae at the expense of blue-green and filamentous algae. (The marked difference between selenite and selenate with respect to the algal forms has been noted above.) Vanadium, probably as vanadyl ion, was not toxic at concentrations up to 5 ppm, but the growth of diatoms versus filamentous algae was favored at very low levels (less than 20 ppb). Similarly, low levels of Cr(VI) (40 to 50 ppb) favored the diatoms, but at 400 ppb blue-green algae completely displaced the diatoms. A shift from diatom to blue-green predominance occurred as borate concentrations approached 1 ppm. Diatom growth was inhibited by 10 ppb Ni(II), but some blue-green species were tolerant to 1 ppm.

DAPHNIDS AND MOLLUSCS

Simple aquatic animals are convenient for testing toxicity in the laboratory and field. Ciliated protozoa (57) and fresh water mussels (306), for example, were used as biological indicators of heavy metal pollution. The toxicity of a long series of metal ions to daphnids was correlated with the negative logarithm of the solubility products of the metal sulfides (46). Heavy metals were divided into two groups according to whether their sulfates were more or less toxic to daphnia than the chlorides (88,89). Artificial water hardness, produced by $CaCl_2$ or $MgSO_4$, decreased the toxicity of Ni(II), Co(II), and Cd(II) to daphnia and fish (474).

In a study of Tabata and Nishikawa (475), complexation with EDTA or thiosulfate reduced the toxicity of Cu(II) to daphnia. A more detailed study by Andrew et al. (14) concluded that the toxicity of Cu to daphnia was directly related to the equilibrium concentration of free or hydrated ion rather than to soluble or total Cu. Cadmium behaved similarly, although it was less completely complexed by NTA; the toxicity of mercury, which was principally in the hydroxide form, was little affected by added NTA or EDTA (188). Similarly, a seawater extract of marine sediments, containing natural chelating agents, reduced the toxicity of Cu to a copepod (292). The citrate complex of Cu, however, was accumulated in aquatic animals (475) and was appreciably more toxic to worms, crabs, and prawns than chromate (384). Insoluble $Cr(OH)_3$ was ingested with marine sediment by a polychaete worm and excreted, whereas soluble chromate ion accumulated to 12 times the concentration in water in a 19-day period (102).

The biological fate of Ru species was studied with the radio tracer ^{106}Ru. Particulate forms were preferentially concentrated by algae, sponges, and ascidians (as compared to soluble forms) (10). A cationic chloro complex was concentrated by clams appreciably more than the neutral or anionic chloro complexes (240). The chloro complexes were accumulated faster by mussels than the NO-NO_3 complexes (253,254).

FISH

Fish, an important economic resource for food and recreation, are particularly susceptible to aquatic pollution. The effects of pollution have been reviewed with respect to freshwater fish (77) and marine animals (496). Some of these effects have been proposed as biological indicators of water quality (48,49,90,301).

The acute effects in fish of high concentrations of different heavy metal ions are generally similar, causing secretion of heavy mucus on the gills and leading to suffocation (95). At somewhat lower concentrations, the ions have different degrees of toxicity and there is considerable interest in extrapolating from a concentration that is lethal to 50% of the population over a 96-hour exposure (LC_{50}-96 hr) to the maximum allowable toxic concentration (MATC) that can be tolerated over the normal lifetime of the animal. The ratio of the latter to the former, called the Application Factor (AF), was expected to be a measure of toxicity nearly independent of the test animal (339). Differences between AF for Cu in hard and soft water (389), and in water containing sewage treatment effluent (76), suggested that the AF should be based on soluble, rather than total, Cu.

The toxicity of heavy metal ions to fish has been related to the inhibition of specific enzyme systems: carbonic anhydrase (104), allantoinase and ornithine aminotransferase (73), and lactic dehydrogenase and glutamic oxalacetic transaminase (GOT) (103). The inhibition of GOT was most sensitive to Ag(I), and Hg(II) and was correlated with the solubilities of the metal sulfides (103). The activity of allantoinase was enhanced by low concentrations ($\sim 10^{-6}$ $\underline{M}$) of Cu(II), Hg(II), Zn(II), and Cd(II) but inhibited by higher concentrations (73).

Chen and Selleck (101) based a mathematical model of the toxic response of fish on the hypothesis of a first-order biological toxic mechanism opposed by a de-toxifying reaction in the organism that is also first-order after an induction period. The critical or threshold concentration of pollutant is the level at which the opposing rates are equal. They studied the effects of Zn(II) and CN^-, individually and combined, on guppies and demonstrated a distinct antagonistic effect between the toxicants. The opposing effects of anion and cation suggest a chemical combination. In Figure 1a the same data are plotted on a mole-fraction basis. The complexes, $Zn(CN)^+$ and $Zn(CN)_2$ are included in Figures 1b and 1c, respectively, in addition to Zn^{2+} and Cn^-. The linearity of response is improved somewhat by inclusion of the complexes, but there is no clear choice between the two additional forms. Both complexes appear more toxic, on a molar basis, than the free ions, but are less toxic on a weight basis. This treatment has been applied by Andrew (13), as well. The kinetics of the uptake and elimination of methylmercury by fish has also been evaluated (209). A somewhat more sophisticated model for multiple toxicants was presented by Anderson and Weber (11).

Elements

Copper-

Because of the wide usage of Cu salts for controlling undesirable aquatic plants, there is great interest in the effects of Cu on fish. Acute toxicity (LC_{50}-24 hr) varied from 1.5 to 11.6 ppm for different Hudson River (NY) fish (385). In this study, the decreasing order of toxicity of ions was Cu(II) > Zn(II) > Ni(II). The LC_{50}-96 hr to fathead minnows in a natural stream was 0.6 to 1.0 ppm, based on the soluble Cu concentration, which was appreciably less than the total added Cu (76). The MATC of Cu for the same fish species in soft water was between 10 and 18 ppb, based on growth, survival, and spawning (339). The MATC, as estimated from 30- to 60-day observation of eggs and fry in soft water, gave values of 5 to 8 ppb for brook trout, and 12 to 21 ppb for channel catfish and walleye pike (403). The order of toxicity in this study was Cu(II) $\sim$ Cd(II) > Pb(II) > Cr(VI). Some fish species responded visibly to these tolerable levels (10 to 20 ppb) of Cu (260): goldfish tended to orient toward the source of a concentration gradient, whereas suckers showed an avoidance reaction.

The toxicity of Cu has generally been observed to be lower in hard water than in soft (339,403,462). This difference has been explained by precipitation by carbonate--the insoluble forms of Cu being relatively non-toxic. Similarly, alkalinity appears to be a controlling factor in reducing toxicity based on total Cu (462). LC_{50} values for minnows in natural water of variable quality were correlated with PO_4 (13,184). Soluble complexes of Cu also appear to be relatively non-toxic to fish. EDTA (348,475) and NTA (458) reduced the toxicity of Cu, and carp grew well in ten times the LC_{50} of total Cu when thiosulfate was added (348). Atlantic salmon tolerated higher levels of Cu in the presence of humic acid, a natural complexant (516). In a study of toxic interactions of some industrial waste components, no interaction between Cu(II) and acetic acid, acetaldehyde, or acetone was found through LC_{50}-96 hr studies of bluegills (92). The toxicity of Cu to minnows was directly related to the activity of Cu(II), as measured by an ion-

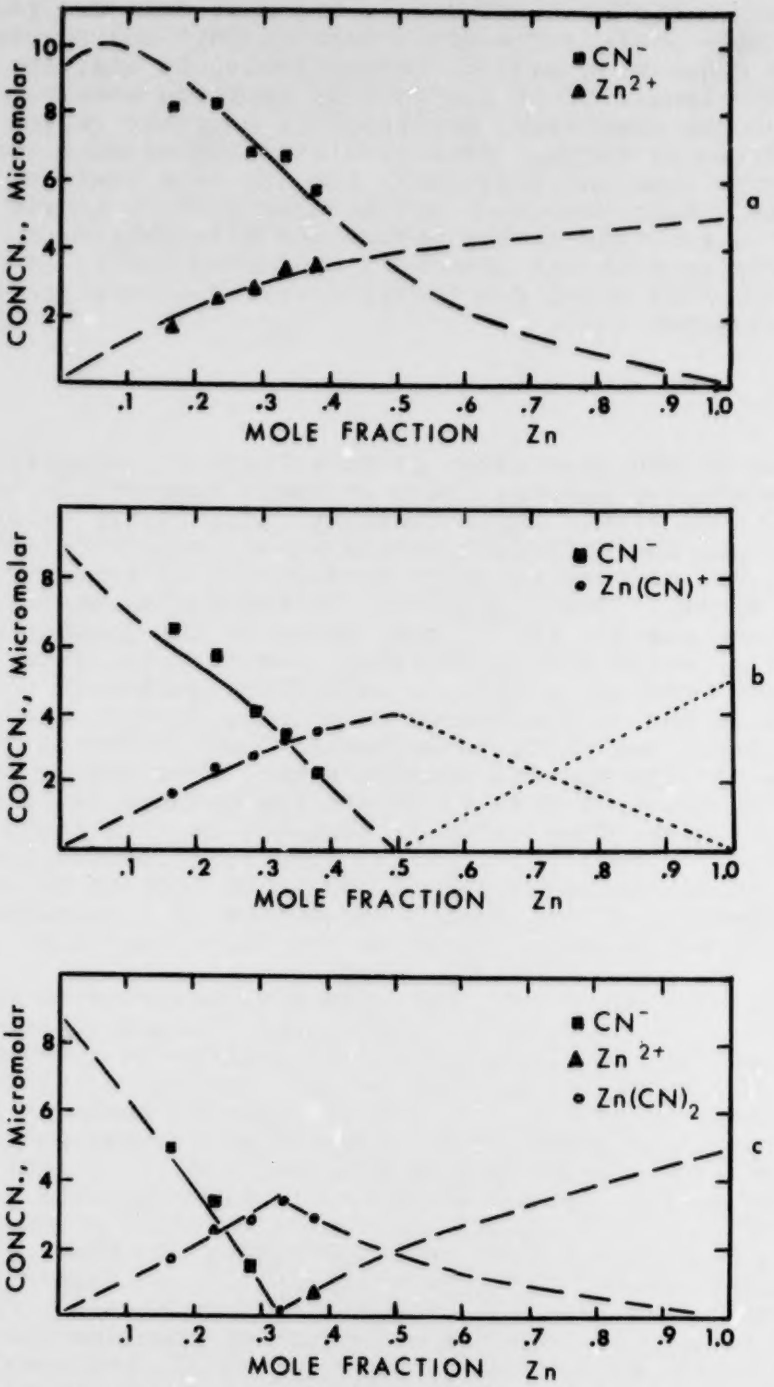

Figure 1. Critical Threshold Concentrations of Zinc-Cyanide Species vs. Mole Fraction of Zinc.

selective electrode (13). Thus, IC_{50} in two different types of water had the same value in terms of Cu^{2+} ($\sim 7 \times 10^{-8}$ $\underline{M}$) but differed four-fold in total Cu concentration (12). Soluble organic or inorganic complexes of Cu were non-toxic (13). An analysis of the forms of Cu in natural water indicated that less than 25% of the total was likely to be uncomplexed at prevalent conditions of bicarbonate and pH (462).

The combined effect of toxicants is important because natural conditions are rarely limited to one pollutant. Several workers have observed than Zn has a synergistic effect with Cu (147,295), the combination being as much as 2 to 5 times as toxic as a simple additive effect (456,459). No synergism was found in another study (91), however. Anionic detergents have also been noted as being somewhat synergistic with Cu (94).

A detailed study was made of the long-term chronic effects of Cu pollution of a natural stream (184). Laboratory tests were made simultaneously using the same water. The laboratory results underestimated the ecological effects over a 5-year period, however, because the avoidance reaction of the fish caused them to select less suitable spawning sites, resulting in lower reproduction.

Cadmium-

The chronic toxicity of Cd to fathead minnows apparently was somewhat less than that of Cu (MATC 40 to 60 ppb) (375) but very similar to Cu in other fish species: 4 to 8 ppb to flagfish (455,456) and brooktrout (403), and 10 to 25 ppb for channel catfish and walleye pike (403). The Application Factor tentatively derived for Cd was much smaller than that for Cu (375) because of the accumulation of Cd in the test animals on long-term exposure. Water hardness decreased the acute toxicity of Cd to several fish species (474) and decreased the chronic effects on walleye pike (403). In one study of a mixture of Cd with Zn and Cu in hard water, the acute toxicity was appreciably greater than would be expected from simple additive effects (147).

Zinc-

The acute toxicity of Zn to native fish species of the Hudson River was measured (385). In flow tests, Zn was more toxic at pH 8 than at pH 6, in contrast to static measurements (337). The speciation of Zn has been discussed in relation to toxicity to fish (364). In chronic studies, the MATC was estimated at 600 ppb for Atlantic salmon (457), less than 250 ppb for bluegills (93), less than 160 ppb for fathead minnows (74), and less than 50 ppb for flagfish (456). Water hardness (337) and NTA (458) reduced the toxicity of Zn. Calcium (91) and, to a greater extent, Mg (515) reduced the toxicity of Zn(II), as did CN^- (92,101). In one study, Zn(II) and Cu(II) were markedly synergistic (457), but this effect was not observed in another study (91).

High concentrations of Zn(II), like Cu(II), attack the epithelial cells of the gills (296). Lloyd suggested that the critical level is that at which the blood can no longer carry the excess Zn away from the site of attack and that this occurs at only twice the normal concentration of Zn in the gill tissue. The effect of Ca(II) and Mg(II) on the toxicity of Zn(II) has been interpreted as a competition for binding to active sites on an enzyme (515). Taking glycine as a model compound, the order of metal binding strengths is Cu(II) > Zn(II) > Mg(II) > Ca(II). Thus, Zn(II) and Mg(II) may be competitive, but Cu(II) is too strong and Ca(II) is too weak to have much effect. The gonad cells of rainbow trout were selectively damaged by Zn(II) (382), concentrations of Zn(II) inhibited spawning in bluegills that showed no other physiological effect (93).

Mercury-

The LC_{50}-48 hr toxicity of Hg(II) to stickleback was 1.7 ppm (325). In contrast, Shaw and Lowrance (426) found 20 ppb for the LC_{50}-24 hr value for the guppy and, further, found approximately the same toxicity for Cu(II). Although the latter report shows a consistent order of toxicity (Ag(I) > Hg(II) Cu(II) > Cd(II) > Zn(II) > Pb(II) > Ni(II)), the lethal concentrations were much lower than found by modern bioassay procedures. Chronic exposure of brook trout to CH_3HgCl over three generations indicated a MATC of less than 1 ppb although there was some indication of acquired tolerance. Mercury accumulated markedly in the tissues at exposure levels that produced no direct toxic effects (326). EDTA greatly reduced the toxicity of Hg(II) (348). Trout removed from an oligotrophic Michigan lake contained more than twice the Hg concentration of fish from a eutrophic lake (138). It was concluded that adsorption of Hg on organic particulates removed the metal ion from the food chain. The toxicity to pike of CH_3Hg^+ (LC_{50}-30 day) was not significantly different when administered as the soluble nitrate or as a protein complex (329). No difference in toxicity to minnows was found between the various inorganic chloro complexes: $HgCl_2$, $HgCl_3^-$, or $HgCl_4^{2-}$ (250).

High concentrations of Hg(II) do not seem to attack the gills in the same manner as Cu(II) or Zn(II) (296). Both $HgCl_2$ and CH_3HgCl were rapidly absorbed through the gills, expecially CH_3HgCl, which was bound to red cells (*in vitro*) (353). Electron micrographs of the gills cf trout exposed to $HgCl_2$ and to CH_3HgCl showed mercury only for the inorganic exposure (354). Methyl mercury may have been lost during the specimen preparation or it may have been carried away by the blood stream. In a study of the effects of 49 compounds on two enzymes in fish blood, GOT was particularly sensitive to inhibition by Ag(I) and Hg(II) (103). Selenite, at close to its own toxic level, reduced the mortality of chubs exposed to acutely toxic levels of mercury (258).

Other Metals-

Aluminum--Suspended Al$(OH)_3$ had lower acute toxicity, but greater chronic toxicity than soluble Al(III) (156). The forms were varied by changing the pH but 50 ppb total Al had no effect at a pH of 7 or greater.

Arsenic--Arsenite was more toxic than arsenate to trout eggs but was rapidly converted to arsenate in aerobic water (119).

Beryllium--The acute toxicity of $BeSO_4$ to guppies was 100 times greater in soft water than hard (441). The LC_{50}-96 hr was lower than the 24-hr value, suggesting a slow or cumulative effect.

Boron--Metaborate was nearly ten times as toxic to young coho salmon in seawater as in fresh water (483).

Chromium--The toxicity of Cr(VI) to eggs and fry of seven fish species appeared to be correlated with length of exposure (403). The estimated MATC for 100 days exposure (150 to 300 ppb) agreed with that observed for 8 to 22 months exposure of brook and rainbow trout (42). The LC_{50}-96 hr values were found for these species (42) and for minnows and goldfish (2). Chronic exposure to Cr(VI) apparently induced some tolerance, and it was suggested that Cr(VI) was less toxic than its bioreduction products (83).

Lead--Lead(II) was about twice as toxic as Cr(VI) under similar chronic test conditions (403) and, like Cr, Pb showed an effect that increased with time of exposure. Acute toxicity, when based on total Pb, was markedly reduced by water hardness (129), but Application Factors based on free Pb(II) were consistent between hard and soft water (128,223).

Manganese--Ordinarily insoluble in oxygenated water, Mn can be dissolved from sediments by the oxygen-deficient hypolimnetic water of deep lakes or impoundments. The toxicity of Mn(II) was apparently lethal to trout at 1 to 2 ppm but was controlled by additions of Ca(II) (235).

Nickel--The MATC of Ni^{2+} to fathead minnows was 380 ppb (greater than for Cu(II), Cd(II), or Zn(II) (374). The toxicity was reduced by addition of $CaCl_2$ or $MgSO_4$ (474). The toxicity of nickel cyanide apparently was due almost entirely to the equilibrium concentration of HCN. On the other hand, silver cyanide gave heavy metal symptoms, probably due to $Ag(CN)_2^-$ (142).

Silver--The MATC of Ag^+ to rainbow trout (0.07 to 0.13 ppb) was determined by using AgI to provide controlled low concentrations (127).

Anions--The anions of As, B, and Cr have been discussed above. Molecular HCN was more toxic than CN^- to fish (142). The MATC of HCN for fathead minnow was 13 to 20 ppb (293), and 5 to 11 ppb for brook trout (263). In a study of a series of copper cyanide complexes, the toxicity increased with the proportion of cyanide, but all were hazardous (294).

Hydrogen cyanide was more toxic at low temperatures and a limit of 5 ppb was not completely harmless to salmonid fish although most warm water species could tolerate 25 ppb (141,263). Some metal-cyanide complexes ($Cu(CN)_2^-$ and $Ag(CN)_2^-$) were major toxicants per se and entered the fish blood, whereas the less toxic $Ni(CN)_4^{2-}$ accumulated in the gills (69).

Chlorine--The effects of residual chlorine on aquatic life have been reviewed (75). Although free chlorine (OCl^-) may be somewhat more toxic and act faster than the chloroamines, there was not a great difference in toxicity between the forms of residual chlorine. A limit of 3 ppb residual chlorine was recommended.

Sulfur species--Molecular H_2S was much more toxic than HS^-, and S^{2-} had completely negligible effects at $pH < 11$ (70,357). The toxicity varied greatly with water temperature and with age and species of fish, but 2 ppb H_2S was recommended as generally safe, except in spawning areas, where the concentration should not exceed 1 ppb (444). Natural H_2S levels can easily exceed these limits, especially in anoxic waters close to organic sediments (37). Although H_2S is readily oxidized by dissolved oxygen, treatment with hydrogen peroxide or permanganate has been suggested as a control measure (235).

The bisulfite ion (HSO_3^-) was 14 times as toxic as SO_3^{2-} to goldfish and 5 times as toxic to guppies (401). The concentration of molecular SO_2 was not significant at lethal levels of the ions.

Nitrogen species-

Unionized NH_3 (or NH_4OH) has long been recognized as being much more toxic to fish than the NH_4^+ ion in equilibrium with it, and a maximum concentration of 0.02 ppm NH_3 was recommended for fresh water aquatic wild life (342). Acute (LC_{50}-96 hr) levels for striped bass and stickleback were about 2 ppm at 23°C in both fresh water and seawater (211). Nitrite (NO_2^-) also is highly toxic, causing methemoglobinemia in fish. Chloride ion had a marked protective effect against nitrite toxicity to coho salmon, however, apparently competing with NO_2^- for uptake through the gills (371).

MAMMALS

The toxicity of metals and their compounds to mammals, including humans, was reviewed in a recent book (302). The point is made that the dose-response relationship rarely shows toxic effects over the entire exposure range. Rather, most substances stimulate growth at trace levels but become toxic at sufficiently large doses. Toxicity is closely related to the electronic configuration of the atom, with elements and valence states in the most stable configuration being least toxic. Those cations that form "soft" acids tend to be most toxic because they form strong complexes with the soft bases of the biological system. An attempt was made in the review to associate carcinogenicity with increasing electronegativity of the element, but there appeared to be numerous exceptions.

Schroeder (413) has made an extensive study of the effects of trace elements in water on the health of rats and mice over several generations. He took elaborate precautions to provide clean air and surroundings and to see that the diet contained minimal amounts of the trace elements. In general, he found that valence state has little effect on toxicity because mammals, in most cases, have the ability to oxidize or reduce an element to a form that can either be utilized or eliminated. On the other hand, he stated that the natural valence state of an element is generally the least toxic form. He made specific comparisons of chemical species of selected elements.

Chromic ion, at 5 ppm in water, was an essential nutrient for both mice and rats. It promoted growth, protected against the toxic effects of Pb and Cd, increased life-span and longevity, and lowered serum levels of glucose and cholesterol. Chromate ion at the same level (5 ppm) had a negative effect on the growth rate of mice (but not rats) and slightly increased the incidence of tumors in mice.

Selenite, at 3 ppm, was highly toxic to rats, reducing growth rate, increasing the incidence of fatty liver, and consistently reducing survival. In contrast, selenate showed none of these effects and greatly increased longevity in rats and mice. Extraordinarily long lives of certain individuals were highly correlated with the selenate diet; however, these aged rats had a high incidence of malignant tumors. In another study, Se(II) apparently induced a high incidence of liver tumors in aged rats (345). It is not clear whether selenate induced the cancers or, by prolonging life, allowed unidentified carcinogens to take effect.

Methylmercury, at 1 ppm, markedly increased the growth of mice but reduced fertility and viability of offspring.

When all parameters were compared in both rats and mice, only three elements were consistently toxic: selenite, Cd, and Pb. Lead, and to a lesser extent Cd, reduced plasma levels of Zn in rats if the diet was deficient in Cu, but nutritionally adequate or excess amounts of Zn, Cu, or Fe protected against Pb toxicity (372). In vitro studies with rat brain tissue showed that Pb(II) and CH_3Hg^+ interfered with metabolic activity similarly at levels below those producing overt toxicity in humans (84). Methylmercury interfered specifically with the conversion of glucose to carbon dioxide. In the same study, alkyltin compounds produced different but equally toxic effects as Pb and Hg. Triethyltin was more potent than dimethyl- or dibutyltin.

Another of Schroeder's generalizations is that the least abundant elements in seawater are the most toxic to mammals because protective mechanisms have not been as well developed in the evolutionary scheme as for the more abundant elements. Figure 2 compares elemental abundances in seawater with the concentrations found in the raw and finished water supplies of U.S. cities. The latter data (265,477) are averages of analytical results, unweighted by volume, and do not include samples in which the element was not detected. Consequently, the values shown tend to be higher than the true average concentrations. Most of the elements less abundant than Al in seawater were found at higher concentrations in drinking water. Data on the toxic effects of compounds containing these elements to mammals and humans have been summarized in exhaustive bibliographies (130,342,343,344). Murthy and Petering (340) found serum cholesterol levels in rats inversely related to dietary, and to serum, Cu levels but unrelated to dietary Zn. High levels of Ca in the diet of rats increased the excretion of heavy metals, providing some protection against the toxicity of Cd and Pb (168), and the simultaneous administration of Zn protected hamsters from the teratogenic effects of Cd (162).

INTERACTIONS OF TOXICANTS

As noted in the cited examples, the combined effects of toxicants are not additive. Although the mechanisms of synergism or antagonism are obscure and need further study (276), some types of interaction are readily understandable.

Antagonism between ions of opposite charge naturally suggests chemical combination. An example is the effect of Zn(II) and CN^- on fish (101) described above. Similarly, the toxicity of cyanide complexes of Cu (295) and Ag (142) depended on the dissociative equilibrium. Selenite in the diet protected rats against the toxic effects of Ag(II) or CH_3Hg^+ added to their drinking water (180). Selenium (form not specified but probably selenite) reversed the inhibition of Hg(II) to the

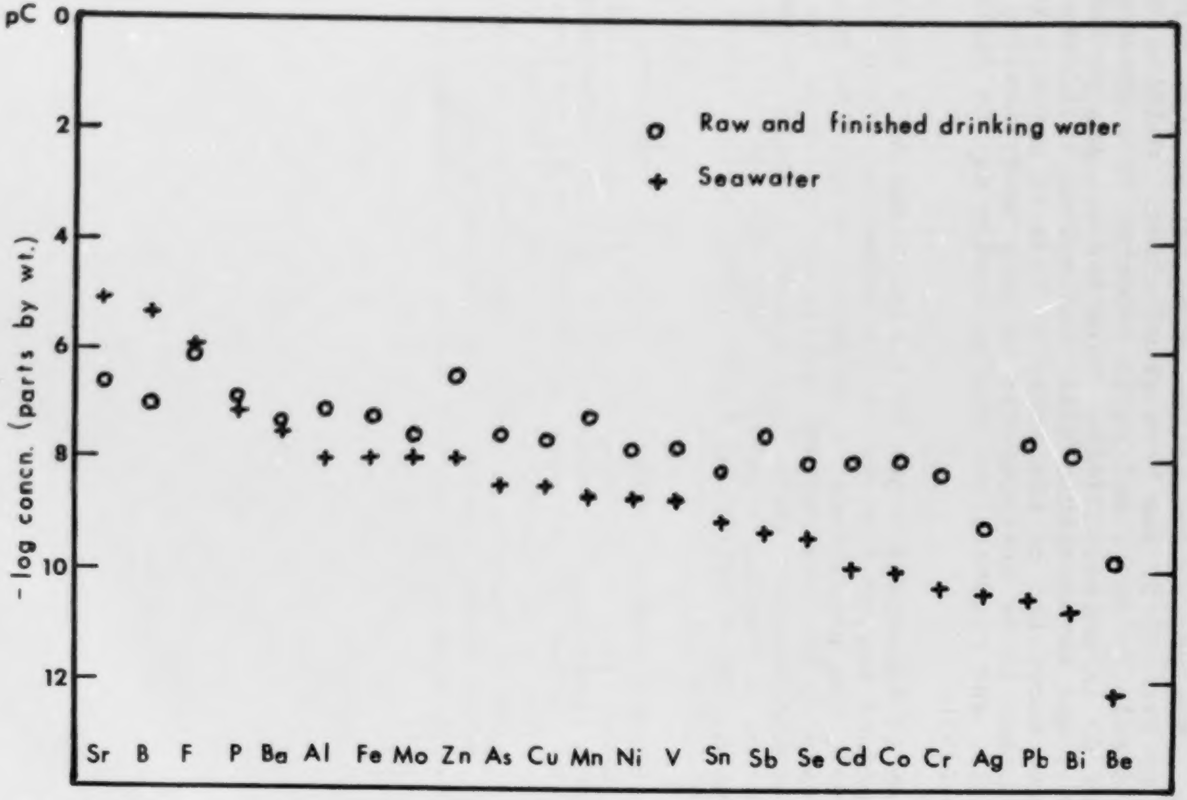

Figure 2. Elemental Concentrations in Seawater and in Drinking Water.

growth of algae (202), and dietary Se protected quail from the toxic effects of methylmercury (179).

Antagonism between ions of the same charge and similar chemical properties may result from competition for the same enzyme system. The protective action of Mg(II) against Zn(II) with respect to fish (515) has been cited above. Calcium and Zn may interact similarly (91), and Zn is reported to counteract the effects of Cd in animals (162). Selenium and As, probably both as anions, are antagonistic (342) and mutual antidotes. Each stimulates secretion of the other in bile of mammals (289). Forms of Se appear to be antagonistic to many heavy metals, including Hg(II) and Cd(366), but the mechanism may be different in each case (391).

Synergism of toxicants might be rationalized as a concerted attack on separate enzyme systems of the organism. On a molecular level, the production of different enzymes in the same organism appears to be interrelated (242); an attack on one enzyme may disable another apart from specific damage to the second by another toxicant. Synergism with the toxicity of Cu(II) to fish has been noted for Ag(I) (454), Cd(II) (459), and Zn(II) (295,457,459).

In a kinetic approach to modeling multiple toxicants, Anderson and Weber (11) developed distinctions between additive and independent responses. Toxicants that had the same response curve (probably acting by the same mechanism) could be treated as a single substance at the total concentration and were called additive; independent toxicants had different response curves unaffected by other constituents. In a test with guppies, Cu(II) and Ni(II) were additive and Zn(II) was independent.

SECTION 5

HUMAN HEALTH EFFECTS

ACUTE VERSUS CHRONIC EFFECTS

Although the acute toxicity of such species as methylmercury (137) in food, chromate in ambient air (342), or cadmium ion in food and drinking water (342) has been forcefully demonstrated following accidental or industrial exposures to unusually high concentrations, the long term effects of trace levels of inorganic species can only be inferred from animal experiments or epidemiological data. The synergistic and antagonistic interactions among trace elements, both as essential nutrients and as toxicants to human health, are complex and little understood (321). The need for water quality data, including chemical species information, for drinking water as supplied to the consumer and for water supplies was recognized in a National Academy of Sciences (NAS) Workshop (20), as a first step in developing epidemiological correlations. A recent report from the NAS (344) thoroughly reviewed the toxicological data and significance of 22 trace elements in drinking water, recommended permissible limits of concentration, and presented the rationale for such limits. Although recommended limits were for the total elemental concentration, in most cases the stable valence ion could be assumed. The possible role of suspended particulates as carriers of trace elements in drinking water was considered, but not enough information was available to assess the significance of undissolved forms. For the present, it is considered appropriate to base drinking water standards on total elemental concentrations for the following reasons:

- The total concentration of an element provides a safety factor, because it includes all species.
- Adequate analytical methodology is not available to characterize drinking water by the inorganic species.
- Epidemiological correlations are based on total elemental concentrations because of the available analytical data.
- Drinking water provides only a small fraction of the total dietary intake of most elements.

- Mammals appear to be quite efficient at interconverting valence states of many elements, so that there is little difference in chronic toxicity of the species.

- For most of the elements of concern, only one species is prevalent in water.

CARDIOVASCULAR EFFECTS

An inverse correlation between human cardiovascular disease and water hardness has been widely noted and reviewed (114,344,502). Although several theories of a cause-and-effect relationship have been advanced, none is generally accepted. Because drinking water supplies less than 15% of the normal intake of any of the elements considered as specific causative agents, the form of the element in water, as opposed to food, would seem to be significant if there is indeed a causal relationship between water factors and health.

ELEMENTS OF CONCERN

Arsenic

Although the acute toxicity of As compounds is well known, the levels ordinarily found in public water supplies are not associated with any adverse health effects (342). The recommended limit of 0.1 ppm in drinking water was intended to provide less than 20% of the normal dietary intake. Inorganic As(III) appears to be the most toxic form, whereas As(V) is the prevalent form in oxygenated waters (342). Arsenite [As(III)] can be methylated in the environment by bacteria to methylarsinic acid, to dimethylarsinic acid, and to dimethyl- and trimethylarsine (504). In addition, a variety of synthetic organic arsenicals are distributed in the environment as pesticides, which can be transported into water supplies. The toxicity of various As compounds is extremely variable (344). A clear epidemiological dose-response relationship between As in drinking water and incidence of skin cancer has been observed, however (237). A thorough and recent review of the health effects of As compounds (344) concludes that the interim drinking water standard of 50 µg/L may not provide an adequate margin of safety and that improvement of speciation techniques for analysis is needed.

Chromium

Chromium is an essential nutrient involved in the metabolism of glucose (422). Only two valence states are ordinarily encountered and the higher [Cr(VI)] is much more toxic than Cr(III). The EPA interim standard for drinking water (490) of 0.05 ppm Cr is based on the carcinogenicity of inhaled chromate dusts (342). Although cancers were induced in rats by the injection of Ca, Zn, or Cr(III) chromates, none were induced by Ba, Pb, or Na chromates or by chromic acetate. The International Agency for Research on Cancer concluded that there is no evidence of hazard to humans from non-occupational exposure to Cr (237). Schroeder (413) found Cr(III) to be an essential trace element for rats and mice that regulates carbohydrate metabolism, lowers serum cholesterol levels, and protects against toxic effects of Pb and Cd. From these studies, he infers that atherosclerosis and diabetes mellitus may be Cr deficiency diseases in humans.

Within the normal hydrogen ion activity (pH) range of surface and drinking waters, Cr(III) is hydrolyzed to its very insoluble hydroxide and is rarely found as a soluble species. Also, inorganic Cr(III) is poorly absorbed from the digestive tract and rapidly disappears from the blood stream after injection (328). In controlled studies (139), less than 3% of an orally administered dose was absorbed by insulin-dependent diabetics. Interconversion between Cr(VI), the stable valence state in oxygenated waters, and Cr(III) can take place under natural conditions (412) and ingested Cr(VI) can be reduced by ascorbic acid taken orally as much as an hour or two later (422). The anionic Cr(VI) penetrates cell membranes more readily than Cr(III) and may bind to erythrocyte globin without undergoing reduction (237).

The NAS review (344) concludes that improved analytical methods are needed for distinguishing the valence states of Cr, especially in animal and plant tissue, and recommends that consideration be given to basing the drinking water standard on the hexavalent form.

Cadmium, Lead, Zinc

Cadmium, lead, and zinc occur in water as divalent ions or complexes of the ions with inorganic or organic ligands. The health effects of the soluble species, however, are considered equivalent to those of the total element. Speciation may be most significant in its effect on the availability of the element in drinking water (20). Surveys of public water distribution systems in Denver (28), Seattle (121), and four locations in eastern U.S. (468) showed that soft, corrosive waters may pick up Cd, Cu, Pb, and Zn between the treatment plant and the home tap. Zinc and Cd were presumed to come from galvanized pipe, and Pb from solder joints in new copper plumbing (121). In older eastern cities, lead plumbing may be a source of Pb in drinking water (114). New copper plumbing contributed soluble Cu only during the first two months of use (28).

Cadmium-

Found only at trace levels in natural surface waters, Cd is a cumulative poison and all sources of exposure need to be watched carefully. The total normal human intake has been estimated at 150 to 400 µg/day (140,228), with a daily accumulation of 3 µg (140). Only about 3 µg/day is supplied in drinking water (20). A survey (145) of dry-weather flows at 720 water supply sites in the United States serving at least 100,000 people showed 4% that exceeded the EPA limit of 10 ppb for drinking water, with a maximum of 130 ppb Cd. The levels appeared to be related to population density. In other work, the sources and significance of cadmium pollution were reviewed by McCaull (324).

Lead-

Human exposure to Pb is probably closer to a critical toxic level than for any other element. Schroeder states that, "no person living today in industrialized societies ... is free of the recondite toxicological effects of lead."(413) This statement is based on the observation that human blood levels of Pb inactivate the enzyme δ-aminolevulinic acid dehydratase (ALA-D) (222) and on the reduction of life span and reproduction of rats fed 25 ppm Pb in their water (413). Lead inactivates ALA-D to a much greater extent than Hg, Cu, or Cd, so the mechanism does not seem to be simple thiol binding (166). Zinc is antagonistic to Pb and the chelation therapy of Pb poisoning that uses Ca-EDTA may lead to Zn deficiency.

Environmental and toxic effects of Pb pollution have been reviewed (428,451). A recent EPA criteria document (492) reviewed thoroughly the health and ecological effects, exposure assesment, and analysis of lead, with particular emphasis on air-borne forms. Lead(II), like Hg(II), binds strongly to sulfhydryl groups of proteins and enzymes and interferes with metabolic processes. It replaces Ca in the bone but can be released under conditions of active Ca metabolism (79). At sufficiently high concentrations, Pb has been associated with at least 25 physiological effects (132). Clinical anemia in children was associated with blood Pb levels greater than 40 µg/dL, central nervous system disorders at 50 µg/dL, and encephalopathy symptoms at 80 µg/dL (492). Unlike most heavy metals, Pb crosses the placenta and blood lead levels in newborn children were closely correlated with those of the mothers (492).

Although drinking water ordinarily supplies less than one-tenth the Pb obtained from dietary sources (344), it is important to control all inputs. Equilibrium calculations indicate that soluble Pb should not exceed drinking water standards in surface waters having moderate carbonate alkalinity

(219). This conclusion was supported by a survey of raw drinking water supplies (145). As delivered at the tap, however, Pb concentrations are more variable and frequently higher. A survey of 969 community water supplies in 1969 showed that 14 samples, on the average, exceeded the 0.05 ppm limit for Pb (323). A survey of Seattle and Boston, where soft, corrosive water was supplied, showed clear evidence of Pb contributed by the plumbing (114).

A NAS review (344) concluded that the interim standard of 0.05 ppm Pb does not provide a sufficient margin of safety, especially for fetuses and young children. Conventional water treatment procedures (either iron or alum coagulation, or lime softening) were effective in removing Pb from water supplies (491).

Zinc-

An essential trace nutrient, Zn is relatively non-toxic. Drinking water provides a negligible fraction of the normal dietary intake (344). The interim drinking water standard of 5 ppm is based primarily on taste preference (342). In a survey of water as delivered to homes in Seattle, 10% exceeded the standard, evidently because of corrosion of galvanized piping (20). Zinc supplied in water was reported to be carcinogenic in rats and teratogenic in rats and hamsters (302). On the other hand, the NAS review (344) found no evidence of carcinogenicity, mutagenicity, or teratogenicity.

The major significance of Zn, with respect to speciation, is its interaction with other trace elements. It is clearly antagonistic to Cd and Pb, both with respect to the toxic effects of the latter elements (166,344,372,422) and to Cd carcinogenicity. Cancer deaths in 28 countries were positively correlated with estimated dietary Zn intake and also regionally, within the United States, with blood Zn levels in healthy subjects (411). The effect was interpreted as antagonism to Se. Little is known about the mechanisms of nutritional interations of elements, but it is not implausible that the chemical forms are critical. Two general approaches may be mentioned: (1) competition on a mass-action basis for active enzyme sites by ions of similar charge, size, and electronic structure (515) and (2) chemical reaction with an antagonist to produce a form that is insoluble or otherwise unavailable (391). A study by the NAS (343) placed highest research priority on the study of the interactions between Zn and Cd and their relation to cardiovascular disease.

Mercury

Since the recognition in the 1950's in Japan and Sweden of the extreme toxicity of methylmercury compounds and the subsequent discovery (246,505) that methylmercury is formed biologically in significant amounts under natural conditions, the environmental impact of Hg has been thoroughly reviewed (137,173,267,269,369). The dialkylmercury compounds, particularly dimethylmercury, are volatile, contributing to the natural cycling of the element, and lipotropic, rapidly passing through cell membranes and becoming incorporated in living organisms. Methylmercuric ion and inorganic cations of Hg are strongly bound to the sulfhydryl groups of proteins and this appears to be the site of their physiological action (160). This implies that any compound or complex of Hg with a smaller formation constant than that of the mercury-protein bond (about 10^{16}) (36) will be toxic. Mercury rapidly accumulates in the aquatic food chain (137). Although mammals can excrete Hg quite efficiently, methylmercury is stated to cause permanent brain damage (413).

Careful studies of Hg concentrations in the Atlantic Ocean showed great variations with depth and location (20 to 1300 ng/L) but the total amount in the sea is too great for human activity to have had a significant influence (393). Numerous studies in both fresh and salt water show that fish tend to accumulate Hg in proportion to both the duration and the intensity of exposure (316). Thus, many pelagic fish have acquired Hg levels close to, or exceeding, the permissible limit for human food.

A survey of 273 community water supplies for Hg showed only 12 with total Hg at or above 1 μg/L (199). There appears to be no hazard from inorganic Hg in drinking water but, until it can be demonstrated that effects on humans of methylmercury is negligible, it was recommended that limits should be set as if all Hg were in the most toxic form (344).

Nitrogen

The EPA interim limit of 10 ppm for nitrogen (as nitrate) is based on the danger of methemoglobinemia to infants (342), probably caused directly by nitrite. A survey of groundwater supplies in rural Wisconsin (135) showed that 40% of the wells exceeded this limit. Nitrate levels in surface waters in Illinois were surveyed and highest concentrations were found in areas of high agricultural production (207). Within a watershed, highest levels occurred near the headwaters and derived principally from inorganic fertilizers. Because so little is known about the effect of nitrate on the general population, this species should be monitored rather carefully.

Selenium

Selenium is an essential nutrient similar to, but distinct from, Vitamin E in its effects (416). It is, however, also one of the most toxic natural elements on an atomic basis. Approximately 0.05 ppm is needed in an individual's daily diet, but 5 ppm is toxic (174). The biological role of Se was reviewed in a 1966 symposium (341) and its significance in water supplies was thoroughly reviewed recently (344).

Differing health effects depending on the form of the element are particularly evident in the case of Se. In foodstuffs, Se probably exists entirely in proteins in which Se replaces S (460). Insoluble selenacious proteins from plants and water-soluble inorganic Se compounds produced distinctly different toxic symptoms in animals (304). Elemental Se is relatively nontoxic but the oxidized forms, selenite [Se(IV)] and selenate [Se(VI)], are extremely toxic. Reports of the relative toxicity of the latter valence states differ according to the test animal and mode of administration. In oxygenated, alkaline water the selenate ion is stable and soluble. In acid waters, however, selenate is readily reduced to selenite, which can precipitate with iron as the very insoluble basic ferric selenite, $Fe_2(OH)_4SeO_3$ (278), limiting the occurrence of Se in water. An important route of elimination in mammals is by methylation to volatile dimethylselenide or dimethyldiselenide, which are exhaled. These compounds, which do not appear to be highly toxic (366), have been identified in the environment as products of bacterial methylation (100).

Although specific animal diseases have long been associated with a deficiency or excess of Se, there appear to be no long-term systemic effects to humans that can be attributed to Se (110,226). Selenium deficiency has been implicated, but unconfirmed, in the Infant Sudden Death Syndrome; excess has been associated with dental caries (343).

Sodium selenite was effective in treating some infant cases of kwashiorkor (primarily, a protein-deficiency disease) in Near Eastern countries but the U.S. diet seems to provide nutritionally adequate amounts of Se (226,422). Although some animal studies have associated Se with cancer (344) and teratogenicity (302), and recent epidemiological surveys found an inverse correlation of cancer deaths with Se intake or blood level (410), the International Agency for Research on Cancer (237) concluded that, "the available data provide no suggestion that selenium is carcinogenic in man, and the evidence for a negative correlation between regional cancer death rates and selenium is not convincing."

To properly assess the role of Se in human health there is a critical need for improved analytical methods to determine chemical forms and valence states (344,366).

SECTION 6

TRANSPORT AND TRANSFORMATIONS

The chemical elements comprising pollutants, of course, can never be destroyed. Inorganic pollutants, much more than organics, are subject to recycling under the influence of natural or artificial processes. Because the harmful properties of inorganic pollutants are often associated with a particular element, such as a heavy metal, the chemical form in which the element is found plays a crucial role in its distribution in the environment and its ecological significance.

The physical and chemical mechanisms available for controlling trace metals in water were reviewed by Leckie (283) and were the subject on an EPA-sponsored conference (118). The role of organic chelating agents in these processes (310) and the effects of dissolved and suspended solids in fresh water (453) were reviewed. Emphasis in the Sorensen et al. study of dissolved solids was on major ions and on salinity as it affects osmotic regulation, however, rather than on toxic effects of trace species. In other work, Gupta and Chen (197) have described a comprehensive analytical scheme for partitioning the trace metals in nearshore marine sediments into seven fractions.

INTERACTION OF WATER AND SOLIDS

Leaching

The mineral content of surface and ground waters and ultimately the sea is derived primarily from the weathering and leaching of rocks and soils. The kinetics of dissolution of mackinawite (FeS) were studied (365). The relation of soil properties to the adsorption-desorption equilibria of certain metal ions was studied (493). The roles of solubility, complexation, and adsorption were discussed in another paper (230) in which the kinetics and equilibria of adsorption of metal ions were studied with respect to four homogeneous solids. In a neutral or acid environment, adsorption was the dominant process controlling the ionic content of the water. Observations of the seepage of effluent water from a nuclear reactor showed that particulate and cationic forms of the radionuclides were strongly retained by the soil, but that soluble nonionic and anionic forms were relatively mobile (394). Factors affecting the mobility of major nutrient anions in soils were identified (249).

The role of aquatic sediments in the cycling and transport of pollutants has been reviewed (271). Suspended sediments are an important mode of movement of adsorbed ionic species, which may later be remobilized by soluble complexants, change of pH, or ionic strength (381). This leaching action led to progressively less-contaminated sediments in the lower courses of a delta (133). Molecular-size fractionation of organics in a stagnating lake system suggested that metals were mobilized from the sediments by low-molecular weight humic substances and then transferred to colloidal particles (407). In this study, Zn was associated with a 0 to 500 molecular weight fraction, whereas Fe, Mn, and Mg were found chiefly in the 10,000 to 50,000 molecular weight fraction. Gel permeation chromatography was used to study complexation equilibria of Cd(II) with organic fractions from lake water (221). The organic coloring matter from several lakes was monobasic, with a mean molecular weight of about 320 (423). This material solubilized Fe increasingly up to pH 10, principally by peptizing ferric hydroxide, although there was some evidence of chelation. Cupric ion was relatively more chelated that peptized.

Sanitary landfills are a potential source of ground water pollution. Leachate from an abandoned landfill exceeded safe levels of Fe, Cr, and Cu; Co and Ni concentrations were borderline (107). Six types of Hawaiian soils were compared for their ability to remove pollutants from landfill leachate (105). Ion exchange was the principal mechanism for altering inorganic concentrations. Montmorillonite was more effective than kaolinite for removing lead from a municipal landfill leachate (195). In a companion study, Pb, Cd, Zn, and Hg were efficiently removed from the leachate by ion exchange on montmorillonite clay (196).

Dredge spoils are another potential source of pollutants through leaching, and a standard Elutriate Test is used to assess the risk. In a study of factors in the test procedure, only the oxygen content of the elutriate had a major effect on the release of contaminants from the sediments (286). In the case of some sediments that were classified as pollutants by the Elutriate Test, only Mn was leached in significant amounts (285). The test showed no release of Hg from a variety of sediments that had been equilibrated with representative coastal water concentrations of Hg (203). Dredging may release toxic amounts of free sulfides, but there is little evidence regarding heavy metals, which are strongly adsorbed on ferric oxides and sulfides (442).

Municipal sewage sludge is another potential source of heavy metal pollution. A literature review failed to reveal any information on the form of elements in the sludge and indicated that the amounts of metal extracted by various procedures bore no apparent relation to the total in the sludge (362). A study of the kinetics and equilibria of heavy metal accumulation on activated sludge showed a relatively high capacity for Pb, Cd, and Hg and much less for Ni and Cr(VI) (346). In two sewage sludges, Cu was more, and Cd less, readily extracted than Zn; 11% and 37% of the extractable Cu in the respective samples was in non-cationic forms (435). The ocean disposal of municipal sewage effluent has been a major contributor of metals to the Southern California Bight (507). The metals were in particulate form or associated with sludge particles. Disposal of sewage sludge on strip-mine spoils, by raising the pH, may release hazardous amounts of molybdate, which otherwise is immobilized by adsorption on the acid spoils (275).

Complexation

The preceding section showed that complexation is one important mechanism for removing metal ions from a solid phase to a solution phase. This section deals with the sources and characterization of significant organic complexants. The interaction of organic chelators and trace metals with respect to transport and transformation processes was reviewed by Siegel (437) for marine aquatic systems and by Singer (439) for fresh waters. "Humic and fulvic acids" are broad terms for classes of organic complexants found in soils and natural waters. Their role in controlling the availability of heavy metal ions has been reviewed (243). Samples from the intracoastal waterway from Charleston, SC, to Norfolk, VA, showed that the fractions of soluble Fe, Cu, Pb, and Zn bound to humic substances were highly variable but generally less than 50% (436). Benes et al. (40) related the interaction of 18 elements with natural humic material from a Norwegian lake to ionic charge and pH. The chemical nature of fulvic and humic acids has been studied in considerable detail (423).

Mercury forms very strong attachment to humic materials in both fresh (406) and sea (469) water. In the analysis of sea sediments for total Hg, the element was not completely released at 500° C (267). Iron and Cu were solubilized by fresh water humic acid primarily by peptizing the ferric hydroxide and chelating the Cu ion (423). In seawater, also, humic acids were effective in solubilizing Fe (373). The complexation equilibrium of Cu(II) with fulvic acid has been studied (178,314). Voltammetric techniques, were used to characterize complexes of Fe(II), Co(II), Pb(II), and Cu(II) with organic fractions from the Great Lakes (318) and to show that the Pb(II) fulvic acid complex is reversibly reduced at the electrode (82).

Carbohydrates and amino acids are also naturally occurring complexants. Metal complexation of carbohydrates was proposed as an indicator of reducing conditions in sediments (331). Seven free amino acids were identified in pond water at concentrations up to a few tenths ppm (518). The metal-complexing ability of sewage and sewage effluent (362) may be related to amino acids or carbohydrates although little has been done by way of characterization. Two distinct molecular weight fractions of sewage effluent were responsible for most of the copper-complexing capacity (38). An equilibrium model for sewage effluent discharged to seawater, under reducing conditions, indicated that only Ni and Co would be appreciably complexed by amino acids (332).

The possible effects of synthetic complexants such as NTA and EDTA has been considered. As little as 2 ppm NTA solubilized Pb from some natural lake sediments (194). NTA, at 1 to 10 ppm, failed to release Cu from a lake sediment that contained 250 ppm Cu (on a dry basis) (400). EDTA was found in domestic sewage effluent (British) at about 170 ppb (181). From published stability constants, EDTA was expected to complex trace metals to a greater extent than amino acids or humic acids but without serious adverse effect.

Adsorption

Adsorption-desorption is an important process in the transfer of metal ions between solid and solution phases. The partition coefficients between river water and suspended sediments were determined for six elements (19). Surface analysis of river sediments indicated that Fe, Mn, Co, and Ni were carried on suspended particles (185). A study of salt-marsh estuaries in the southeastern United States showed that the Fe and Mn content of the river was deposited almost quantitatively in the estuary by settling of sediments and flocculation of organics (501). Increasing salinity in the estuary displaced adsorbed Cd, Zn, and Mn, but not Hg. A survey of Hg in the LeHave River (Nova Scotia) showed that soluble Hg was rapidly discharged to bottom sediments downstream from the municipal source, but the Hg associated with suspended particles increased sharply with salinity in the estuarine zone (113). The strong binding of Hg by marine sediments, noted above, is probably a form of chemisorption rather than physical adsorption. Significant differences between concentrations of As, Cu, Hg, and Zn in surface and deep sediments from Lake Superior were found when the analyses were based on the very fine (less than 2 μm) fraction of the sediment (213). Fine particles have been noted as both source and sink for nutrients and pollutants in the estuarine environment (414).

The adsorption isotherms of Pb(II) (390) and of Zn(II) (429) on soils have been measured. The equilibrium amount of Pb(II) retained was substantially greater than the ion-exchange capacity indicating that another mechanism was involved. Although the data could be fit by either Freundlich or Langmuir-type isotherms, the derived energy terms were not consistent (452). From the measured ion-exchange capacity of a synthetic clay it was estimated that 90% of the Pb in surface waters might be adsorbed (218). It was difficult to extrapolate to natural stream sediments. The negatively charged hydrous surfaces of feldspar and similar minerals form active sites for the adsorption of cations and account for the marked influence of pH (361,367).

Aluminum, Fe, and Mn play a significant role in the distribution and transport of trace elements because, under appropriate conditions of pH and oxidation state (Fe(III), Mn(IV)), ions of these elements form hydrous oxide precipitates that have large specific surface areas and strong adsorptive capacities. This function has been discussed in terms of controlling conditions, particle size, and effects of organic ligands (210,245,247,284,406). The transformation of hydrous aluminum (450) and ferric oxyhydroxide (282) precipitates to an equilibrium crystalline mineral phase is extremely slow. Iron-59 was a useful radio-tracer for following suspended sediments in rivers (405). The precipitation of Al^{3+} (229) and Fe^{3+} (165,257) with phosphate has been studied. Three forms of P in surface sediments in Lake Erie sediments were identified: (1) natural mineral apatite, (2) organic P, and (3) inorganic P associated with amorphous hydrated ferric oxide (497). As examples of the influence of these solid phases, the elementary analysis of plankton from widely separated ocean areas suggested that trace metals were transported by adsorption on fine (< 0.2 μm), Fe-rich particles trapped by the plankton (488). The As content of the sediments of Lake Washington (WA) was strongly correlated with Fe and Mn (115), as was the phosphate cycle in Wisconsin lakes (33). The seasonal variation in the soluble and particulate Fe transport to Lake Tahoe (NV) was recorded (152).

Organic particulates also sorb and transport, or immobilize, metal ions. There probably is no clear distinction in this case between chemisorption on the particulates and complexation of the metals with surface ligands. This process has been related to organic sediments in a stagnating lake (407), to the association of Hg with suspended solids in sewage treatment effluent (261), and to adsorption on bacterial cell flocs as a means of removing trace metals (143). The release of trace metals on dilution of sewage sludge with seawater was studied experimentally (395). Under aerobic conditions Cd, Cu, Ni, Pb, and Zn were released to the greatest extent through processes of oxidation, desorption, and complexation.

A study of the adsorption of Cu(II), Zn(II), Pb(II), and Cd(II) on four synthetic solids chosen to represent various soil types concluded that adsorption is the most important process in the soil-water system of a neutral or acid environment (230). Similarly, Stumm and Bilinski (470) concluded, for natural systems, that the dominant fraction of metal ions is associated with particulate and colloidal material and that the strong effect of pH on adsorption results from its effect on speciation. The variation with pH of adsorption of Cd, Cu, Pb, and Zn on clays indicated that the least soluble species were cationic hydroxy complexes, rather than the neutral hydroxides (158). Organic ligands affected the hydrolytic equilibria but did not necessarily reduce adsorption. The sorption and release of trace metals from fly ash was investigated (480). The alkalinity of the fly ash was related to its Fe/Ca ratio. The movement of trace metals across the interface between seawater and sediments has been discussed as a function of oxidizing or reducing conditions (300).

Adsorption processes have been proposed for the removal of metal ions in waste treatment. The addition of organic ligands improved the surface potential for adsorption on carbon of Cd(II) (231). Conversely, Fe coagulation improved the adsorption of some organic complexants on carbon (495), and Ca(II) improved the adsorption of viruses on sand, probably by charge neutralization (244).

BIOGEOCHEMICAL CYCLING

Mercury

The natural cycle of Hg, which has been studied more extensively than that of any other heavy metal, has been discussed in several reviews (137,157,183,267,469). The principal features are indicated in Figure 3, which is derived from many sources. The element and its compounds are relatively volatile and a major release from the earth to oceans (393) and atmosphere (267,269) is by evaporation and volcanic activity. The major mercuric minerals are forms of HgS, which is extremely insoluble and refractory. Weathering and erosion make the mineral available to soil bacteria (137,173), which can metabolize HgS to elemental Hg (5) or to organo-derivatives (5,108,138). Dimethyl mercury is very volatile and escapes directly from the soil or sediment. Methylmercuric ion, like the simple mercuric ion, is strongly complexed to thiol groups of protein-derived organics and undergoes exchange between soluble and particulate complexes (36), indicated as "RHg-Organic" in the figure. These ions and the elemental Hg also experience strong physical adsorption to mineral particulates ("Partic." in the figure), and fallout with dust is a major mechanism for the removal of Hg from the atmosphere (267). In the aqueous phase, mercuric ion is the stable species under usual conditions, and elemental Hg is oxidized (215). The mercuric ion (represented as Hg(II)) is largely complexed with inorganic ligands in aqueous solution (17,215). Bacteria and other aquatic biota transform mercuric ion to the elemental form (109,383) or to methylated species (108). Mercurous ion may be an intermediate in several of these processes but it does not seem to be a persistent or abundant entity. Although industrial

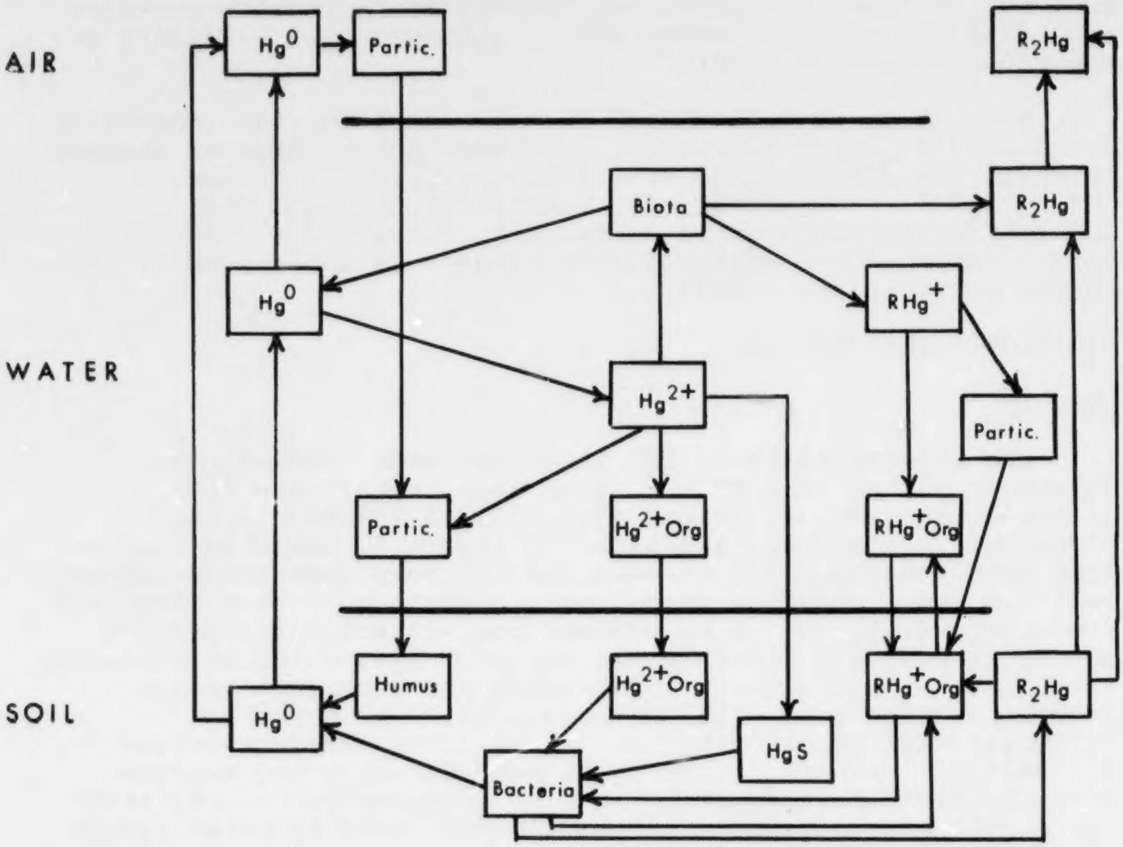
AIR
Hg^0
Partic.
R_2Hg
Biota
R_2Hg
Hg^0
RHg^+
WATER
Hg^{2+}
Partic.
Partic.
$Hg^{2+}Org$
RHg^+Org
Humus
$Hg^{2+}Org$
RHg^+Org
R_2Hg
SOIL
Hg^0
HgS
Bacteria

Figure 3. Cycle of Mercury in the Environment.
(R represents the methyl group, primarily.)

activity has created severe local disturbances in the cycle, it has been completely insignificant on the global scale (267).

The possibility of biomethylation of elements other than mercury was considered (404,504): As, Se, Te, and S were the most probable candidates (see further below).

Iron

As has been indicated, the chief ecological significance of Fe is in the formation of colloidal or fine amorphous particles that have great adsorptive capacity for trace elements. In a Lake Erie study (85), about 95% of the Fe was bound to inorganic particles and was in equilibrium with the water; very little Fe(II) appeared to be released from the lake bottom. The particle size and aggregation of Fe with organics was a function of circulation in a lake (3). The chemical mechanism of ion adsorption on freshly formed ferric hydroxide precipitates is poorly understood (472). The solubility of Fe species is strongly dependent on pH, redox potential, and complexation (217). Fe(III)-OH precipitates are very insoluble and only slowly are transformed to stable crystalline forms (282). Over a wide pH range, Fe(II) also forms basic phosphate precipitates of indefinite stoichiometry (257). The solubility of Fe(II) in hydroxyl-carbonate systems was redetermined because of errors in classical thermodynamic data (440). Many organic compounds were strongly complexed to Fe(II) and inhibited its oxidation although oxygen was taken up by the system (479). Similarly, the Fe(II)-Fe(III) couple was effective in oxidizing organic matter, which was oxidized completely before the Fe(II) (248). Iron is also an essential nutrient for phytoplankton and apparently must be in a soluble, organo-complexed form to be nutritionally available (290). The addition of EDTA was effective in stabilizing the soluble Fe(II) content of seawater against loss by adsorption on the walls of the container (291), and natural complexation was proposed to control the adsorption equilibrium in seawater. On the other hand, most Fe(II) was present as uncomplexed Fe^{2+} in anoxic bogwater (224).

Manganese

Like Fe, Mn is significant for forming fine precipitates that carry trace materials by adsorption. In oxygenated waters, only negligible amounts of dissolved Mn are expected because of the low solubility of Mn(IV) oxides. Nevertheless, Mn(II) was reported in Kansas streams in approximate solubility equilibrium with the divalent hydroxide or carbonate (18). In anoxic sediments, Mn is resolubilized by reduction more readily than Fe (136). Lake Erie sediments released Mn(II), which remained in solution at less than 50% oxygen saturation (85). The reduction process may be biological (378) or may represent direct reaction with organic matter (236). Organic complexation may be a factor in solubilization (378). In Arctic lakes, Mn was largely associated with organic ligands (32).

Selenium

The natural cycle of Se has been reviewed by Lakin (277). Volcanic action releases Se principally in the atomic form, which is oxidized to SeO_2. Either elemental Se or selenite is stable in water, depending on pH and oxidation potential. It is precipitated principally as the very insoluble basic ferric selenite. Biological methylation of Se in bottom sediments yields at least three volatile compounds: $(CH_3)_2Se$, $(CH_3)_2Se_2$, and one of unidentified composition (100). Bacterial ozidation of CuSe to Se^0 has been identified (485).

Arsenic

The As cycle in natural waters was reviewed in broad terms (161) and studied locally in Lake Washington (WA) (115). In that location, the sediment levels of As were correlated with the operation of a nearby copper smelter. The input to the lake was approximately equally divided between atmospheric and surface water sources. Two-thirds of the input was in the arsenate form but 55% of the As in the sediment was arsenite, with a few percent as dimethylarsinic acid. Arsenic was carried to the sediments by association with Fe and Mn precipitates. The methylation of As has also been observed in Florida soils and surface waters (63). The chemical pathways for biomethylation of As have been reported (111,322,504).

DISTRIBUTION OF ELEMENTS AND SPECIES

Closely related to the determination of the cycle of forms of an element through the environment is the distribution of all chemical species within any body of water. The principles controlling the equilibria and kinetics of chemical and biological transformations have been the subject of books (471), chapters (283,334,470), and journal articles (39,398). The sources, distribution, and effects of trace elements in the aquatic environment were also the subject of a recent literature review (287). In the following sections, chemical characteristics are considered for major types of natural water bodies.

Rivers and Streams

Moving, fresh waters generally have relatively low dissolved mineral content and moderate to high oxidation potential. A major transport agent is suspended sediment, either mineral or organic, which can carry trace elements by adsorption or complexation.

A nation-wide survey of surface waters serving municipal supplies showed many instances of soluble heavy metal content exceeding drinking water standards (265). Although soluble Zn frequently, and Cd occasionally, exceeded the standard, these ions were generally well below the equilibrium solubility limits for the stable solid phases (216). On the other hand, Pb concentrations, which rarely exceeded drinking water limits, were close to the calculated solubility saturation in many samples (219). The percentage of total soluble elements in Susquehanna River (NY) water that was exchangeable on Ca-Chelex 100 resin decreased in the order Cd > Pb > Zn > Cu (163). Similarly, anionic and cationic exchange properties of elements in the Cape Fear basin (NC) were studied (430). As expected, Cr(VI) was almost completely anionic, but Cr(III) was mostly particulate, with 37 to 49% distributed among anionic, cationic, and soluble non-ionic forms.

River sediments are less contaminated with heavy metals toward the mouth because of leaching or resuspension by organic complexants (133). As a corollary, mountain streams high in humic substances may have a high content of soluble metals (494,498). The upper reaches of the Susquehanna River, in fact, had an unusually high fraction of soluble metals, although the total loading was low, and the organic ligands were 94% saturated with metals (150). The decrease in soluble metals toward the mouth of the Cape Fear River was not accounted for by dilution, but probably by chemical precipitation (430). In organic-rich river waters of Puerto Rico, only 44% of Cu and 75% of Zn was organically complexed, probably because of competition with Ca(II) (330). Calculation of the speciation of 2 ppm total Cu in natural fresh water indicated very low levels for the free ion (473).

Heavy metal levels of Ottawa and Rideau River (Ontario) sediments were correlated with surface area, suggesting an adsorption mechanism, but the correlation was poor for Pb and invalid for Hg (352). Streams receiving mine drainage may have high levels of dissolved metals because of the high acidity resulting from the oxidation and hydrolysis of Fe(II) (380).

Lakes and Impoundments

The low flow velocity in lakes permits deposition of much of the entering suspended solids. The sediment of an eutrophic lake was a sink for Hg, Cd, Pb, and Tl (316). The solubilization of metals from the bottom sediments may be mediated by organic complexation or by the usual large vertical gradient of oxidation potential. Depending on depth and latitude these bodies are subject to seasonal mixing or overturn as a result of varying surface temperatures. Copper and Mn in the Denver water supply were related to the overturn of the reservoir (28).

A solubility equilibrium model for the Great Lakes (268) indicated that the cold waters contained excess CO_2 and were unsaturated with respect to calcite, dolomite, and apatite, although the warm waters were supersaturated with these minerals. Another model for Cu, Ni, and Zn in Lake Michigan (499) concluded that concentrations of Zn could be accounted for by natural sources, whereas Cu and Ni were largely derived from man-made pollution. A model was derived for the transport of Zn, Pb, and Cd and their deposition in the sediments of a reservoir (376). The transport of heavy metal cations in both surface and groundwater was studied in the Perch Lake basin northwest of Ottawa (29). The roles of Mn (136,378) and of Fe (33) in the composition of lake sediments have been studied. The cycling of Fe and Mn in Lake Erie (85), of As in Lake Washington (115), and of Mo in the Dillon Reservoir (CO) (68) have been discussed.

The organic complexation of Cu, Pb, and Cd has been studied in the Great Lakes (318). The speciation of 18 metals with 8 cations and 4 organic ligands was computed for the concentrations found in Lake Superior (188). Seasonal variations in the ionic Cu concentrations in a pond were related to organic complexants (259). The speciation of Cu(II) in Torch Lake (MI), notoriously polluted by mining operations, was investigated to account for the tolerance of algae and fish to unusually high concentrations of soluble Cu (297). The interaction of metals and organics has been investigated in stagnating lakes and bogs of the Temperate Zone (224,377,407) and in the Arctic region (31,32).

Estuaries and Bays

The large gradient of ionic strength as fresh waters merge with the sea leads to flocculation of much of the organic burden and precipitation of the heavy metals complexed or adsorbed thereon (501). Some metals may be redissolved as chloride complexes. The high organic content of bottom sediments and poor circulation of water frequently leads to anoxic conditions at the bottom of lagoons, with the biological production of sulfide, which ties up heavy metals (484). In the New Bedford (MA) harbor, Cu was associated with the very fine top sediment ($< 2\ \mu m$) and decreased in concentration exponentially from the industrial source to the sea (464). Selective leaching showed that Cr was associated with a different sediment fraction than Cu or Zn. The diurnal cycling between oxidizing and reducing conditions on tidal flats has induced marked cycling of S and Fe (37). Salt marshes appear very effective at removing heavy metal pollutants, at least until their capacity is exceeded (434,500). Metals whose distribution and chemistry in the coastal environment have been studied include Hg (113,134,500,501), Pb (134,434,484), Cd (501), Cu (134,484), Zn (61,239), and Mn (193,484). The fate of trace elements was reviewed (159) and the requirements of a comprehensive model were summarized (503). A surface complexation-adsorption model successfully accounted for the removal of trace metals from the aqueous phase in the Delaware Estuary (472).

Oceans

The outstanding feature of seawater is the remarkably constant elemental composition in all oceans. This implies a mixing time, (somewhat less than 1000 years (58)) appreciably shorter than the times of major geological processes that determine the ocean's composition. Much effort has been given to developing models to account for the composition of the sea because these would shed light on the geological history of the planet. Sillen (438) concluded from an equilibrium model that the pH of the ocean, and hence its CO_2 solubility, is determined by the formation of silicate minerals. A comparison of equilibrium solubility data for oxide and carbonate minerals in seawater with sedimentation rates indicates that the sea is more accurately represented by a steady-state model, rather than an equilibrium model (408). Given the elemental composition of the oceans, equilibrium species of the minor elements have been calculated (146,189).

Refined analytical techniques have revealed significant variations in concentrations of trace elements with depth and location (393) and more attention is being given to the determination of species. Copper in surface waters exists chiefly as soluble organic complexes (7,347) although $CuCO_3$ is the major soluble inorganic form (389) and the deep waters apparently have a relatively high concentration of free Cu^{2+} (347). Similarly, soluble, inorganic Zn in surface waters is present chiefly as $ZnCO_3$ or $Zn(OH)_2$ (510,514).

SECTION 7

ANALYTICAL METHODOLOGY

Ideally, analytical methods for inorganic species in water should determine all the distinguishable forms without altering the composition of the sample in the process of measurement. This, clearly, is an extremely difficult goal because, for many elements of interest, the total amount is at trace levels and because many of the species of interest exist in labile equilibrium that is subject to shifting with almost any manipulation of the sample. Studies of the effects of speciation have been based on analytical methods that were far short of the "ideal". In fact, "species" are defined operationally by the methods used to determine them, which may be no more sophisticated than a distinction between "soluble" and "insoluble" or "other" forms of an element.

Approaches to the solution of the analytical problem fall into three categories, dicussed in the following sections:

- Calculation of thermodynamic equilibria. In this case, the species are defined independently but their concentrations in a real sample can only be inferred.

- Direct measurement of a physical or chemical property associated with some portion of the total element in a sample.

- Separation of the sample into fractions by physical or chemical means, followed by total elemental analysis of the fractions.

The problems, pitfalls, and special considerations involved in the analysis of environmental water samples have been reviewed (65,165,393), both with respect to trace concentrations of elements and to particular species.

A recent review (34) deals with the sampling, preservation, and concentration of environmental waters; another (144) is concerned with the determination of trace concentrations of elements and species in microsamples (< 1 μg). Thorough and recent literature reviews of analytical methods (167,431) deal principally with "total element" methods but include direct techniques for species. Florence and Batley (171) reviewed analytical methods for the forms of Cu, Pb, Cd, and Zn in natural waters and proposed a speciation scheme.

EQUILIBRIUM CALCULATIONS

Thermodynamic methods, combined with equilibrium data for such processes as solubility, complexation, or chemical reaction, enable the calculation of the phases and species that can coexist in equilibrium under specified restraints of temperature, pressure, total concentration, etc. The application of these techniques to environmental waters is described in detail in such texts as that of Stumm and Morgan (471) and the review by Kemp (256). Procedures for the determination of stability constants have also been reviewed (399). Because equilibrium constants are necessarily experimentally derived, the methods, in effect, are a means of extrapolating from laboratory conditions, in which the species can be accurately identified and measured, to assumed field conditions. The methods also permit the use of measurable parameters of the field sample (temperature, pH, dissolved oxygen, total elemental composition) to estimate the difficult-to-measure species that can be present. The use of evaluated thermodynamic data to calculate ionic equilibrium constants was emphasized (461).

Mathematical models are useful only to the extent that they successfully predict conditions in the real world. The assumption of equilibrium is most often the major limitation of thermodynamic models. More sophisticated calculations take into account the rate at which key processes in the model proceed, but suffer from a dearth of reliable kinetic data. All models are simplifications, neglecting factors that are unknown or assumed to be negligible. Consequently, their validity must be checked independently.

Among the environmental applications of thermodynamic models, the U.S. Geological Survey papers on solubility relationships are noteworthy. These include data for Hg (215), Pb (219), Cd and Zn (216), Al (214), and Fe and Mn (217). Hydrolytic equilibria of metal ions were reviewed comprehensively by Baes and Mesmer (22). The inorganic and metal-organic species in Lake Superior were calculated for 18 metals and 12 ligands (188). The chemical speciation of Cu has been calculated for a great variety of conditions and compared to analytical determinations (22,313,389,473,513). The speciation of elements in seawater has been calculated from thermodynamic models (146,189,198). The significance of kinetics in precipitation reactions has been treated (408,489) and the problems in modeling complexation reactions were discussed (151). The chemisorption of cations on ferric hydroxide precipitates was successfully modeled (472). It has been suggested (54) that calculation of metal-cyanide equilibria is the only way to estimate the species composition without disturbing the equilibrium.

DIRECT SPECIES DETERMINATION

Electrochemical Methods

Potentiometry-

Measurement with ion-selective electrodes (ISE) is the only practical potentiometric technique. The familiar and extremely useful measurement of pH is included but ions other than hydrogen are of more interest here. ISE measurement methods all have the outstanding advantage of providing a rapid, fairly direct, *in situ* measurement of a free ionic species without altering the sample appreciably. They can also be used as indicators in potentiometric titrations, in which case the sample is changed. The term "free ion" may need some definition. There is reason to believe that no bare, atomic cation exists in water, all being solvated more or less strongly with water molecules and possibly complexed with hydroxyl or other very labile ligands. Nevertheless, there is no evidence that any ionic species that gives an ISE response behaves otherwise than as a "free" ion in biochemical or geochemical processes. Some disadvantages and limitations are common to all ISE methods:

- A properly functioning, reversible reference electrode is needed. The potential difference is measured between this electrode and the ISE.
- The measured potential is a function of the thermodynamic activity of one or more substances involved in the electrochemical cell reaction. To relate the measurement to the activity of one ionic species requires an extra-thermodynamic convention that cannot be applied to calibration and measurement in real systems without invoking assumptions or approximations.
- To relate ionic activity to concentration requires knowledge or control of the ionic strength of the solution, information that may be difficult to obtain in polluted or brackish water.
- The logarithmic response of an ISE to ionic activity gives it an approximately constant relative error. At higher concentrations, this tends to put ISE techniques at a disadvantage with respect to other analytical methods that have a nearly constant absolute error.
- All ISEs are more or less subject to interference from other ions.

- Only a few commercial ISEs have detection limits below one part per million.

Applications of ISEs in environmental research have been reviewed (279,312,392), as have more general applications (266,356).

As endpoint indicators in potentiometric titrations, ISEs have been used to determine ionization and stability constants for use in equilibrium models. For example, the dissociation constants of carbonic (327) and boric acids in seawater were measured (206) and the speciation of Fe in seawater was studied (87). The Fe(II) ISE was used to determine the stability constant of $FeHCO_3^+$ (440). Attempts to measure complexation constants and hydrolytic equilibria of methylmercury were inconclusive (280,281). Considerable structural information about fulvic acid was obtained from potentiometric titration (177).

The direct potentiometric measurement of ion activity has been studied more extensively for Cu(II) than for any cation other than H^+. Conventional ISE techniques are suitable for free Cu^{2+} measurement at greater than about 50 ppb (446,463), but special precautions are needed to obtain reliable measurements at 10 ppb (447). These include polishing the electrode surface (50), removing adsorbed Cu ions with acid (50) or EDTA (12), using an antioxidant (12,447), avoiding light (12,447), and providing steady flow rate past the electrode (50,386). Reproducible measurements of 2 ppb Cu^{2+} in seawater were made with a non-Nernstian response (387). In this study the electrode was leached with seawater until CuS was removed from the surface of the electrode, which approached a Ag_2S electrode in response and gave mixed potentials to copper. Laboratory measurements of Cu^{2+} were extended to about 0.05 ppb by following the rate of change of potential of an electrode that had been carefully preconditioned (50). The response to Cu^{2+} of the chalcocite crystal was compared to that of the synthetic sensing membrane (233), and various commercial electrodes were compared in buffered Cu(II) solutions (204).

Studies with the copper ISE have been used to determine the toxicity of Cu^{2+} to algae (445), to demonstrate that the free ion is the species toxic to daphnia and minnows (13), to relate Cu toxicity to salmon to humic acid levels (516), and to monitor the Cu^{2+} species in continuous-flow fish bioassay tests (313). In a complete analytical scheme for the speciation of Cu (462,463), the Cu ISE was used for the free ion. Direct determination of Cu^{2+} in seawater by ISE was considered more reliable than extraction of the Cu diethyldithiocarbamate complex (252). The Cu ISE was used for the indirect determination of Fe(III) (176) and in the chelometric titration of metals (355).

Other ISE techniques that have been evaluated for environmental use include the CN electrode (350,409), which gave a Nernstian response to greater than 0.25 ppm CN^-. The nitrate electrode was subject to some interferences that could not be compensated (311). In another study, NO_3^- was determined by ISE with an error of less than 2 ppm (334). The nitrate electrode was applied successfully to sewage treatment effluents and nitrification plant process streams (509). The Ca electrode was used to measure adsorption of Ca^{2+} on hydrous iron oxide (363); phenolic compounds interfered. Measurements of Cd in soil extracts by ISE and by atomic absorption spectrometry (AA) were in close agreement for more than 50 ppb Cd (241). The determination of Na and K in alpine streams was considered more reliable by ISE than by AA because the electrodes did not respond to suspended solids (386). The complexation of Cu and Pb with humic and fulvic acids in natural waters was studied using ISEs (81).

Gas-sensing electrodes are discussed under Physical Separations, because the distinctive feature is a semi-permeable membrane that selectively passes gaseous species. The potentiometric response then derives from ionic species in the electrolyte filling solution.

Voltammetry-

Voltammetry refers to the measurement of current in an electrochemical cell under controlled potential, and the technique includes variations of polarography. Because of the finite current, determined by the extent of faradaic reaction, the cell is not at equilibrium, the concentration at the electrode surface is usually not the same as in the bulk of the sample, and the measured current often includes non-faradaic components. Nevertheless, the procedures can yield useful analytical data on species without altering the sample significantly. Newer techniques such as pulse or square-wave polarography substantially eliminate non-faradaic current components so that the measurement is directly related to a concentration of electroactive species. Under the usual diffusion-limited conditions the maximum current is proportional to the bulk concentration of the diffusing species that controls the electrochemical reaction. These species are usually "free" ions or labile complexes. The term "free" is used in the same sense as with ISE. Complexes are designated "labile" or "non-labile" qualitatively depending on whether they dissociate rapidly enough to provide an equilibrium concentration of free ions at the electrode surface during the period of measurement, which may vary in the range of milliseconds to minutes. Complexes can also be distinguished as "strong" or "weak" depending on their stability constants. The smaller the proportion of free reducible cations in equilibrium with the complex, the more negative will be the potential at which the reduction current reaches its maximum, or diffusion-limited, value, in accord with the Nernst relation. A scheme has been proposed (359) to distinguish, at least qualitatively, among free ions, strong and weak, labile and non-labile complexes using current and potential measurements and titration with free ions or ligands. A comprehensive scheme for the speciation of trace metals in fresh water uses anodic stripping voltammetry (ASV) in combination with ion exchange and ultraviolet destruction of organic ligands (170).

Despite the somewhat qualitative and subjective interpretation of voltammetric data for complexes, the techniques are extremely valuable for the determination of free or labile forms because of a considerable degree of specificity and high sensitivity. Linear sweep voltammetry (LSV) is a rapid procedure with a detection limit of about 10^{-7} $\underline{M}$ (305). Differential pulse polarography (DPP) has a detection limit of about 10^{-8} $\underline{M}$, whereas ASV, which involves electrochemical preconcentration, can determine 10^{-9} $\underline{M}$ or less (9), especially in combination with LSV or DPP. Among the variations and newer techniques that may prove advantageous are programmable voltammetry (320), automated pulsed current voltammetry (220), and semi-differential electroanalysis (120,191). Controlled-potential deposition on graphite was used to separate ionic species; the total metal deposited was then determined by X-ray fluorescence (56) or by atomic absorption spectroscopy (35).

The ASV technique, using thin mercury films supported on solid electrodes, is favored for trace analysis because of its great analytical sensitivity, but is has limitations. The procedure is essentially limited to the ions of metals that form amalgams, with a few exceptions (26,319). It is also subject to intermetallic interferences (182). The significance of these effects in the analysis of seawater has been studied in considerable detail (64,417). All voltammetric methods at mercury electrodes are subject to more or less interference because of the adsorption of ligands or surface active materials on the electrode, and this effect seems especially severe with ASV (26,155,318). The specific interference of a wide variety of natural and model organic compounds has been reported (66). Adsorption effects have been turned to advantage, however, by using the capacitive current to study the adsorption of fulvic acid and its interaction with Pb (82). This application was more a research tool than a practical analytical method for environmental samples, however. Organics strongly adsorbed on pyrolytic carbon electrodes were determined directly by DPP (72). Fast Fourier Transform of faradaic admittance was suggested as a method for monitoring ASV techniques for abnormal quasi-reversibility or surfactant interferences (415). ASV and direct DPP measurements were combined to demonstrate that adsorption was not a serious interference in measurements of carbonate and glycine complexation (8,155). Studies of the competition of Ca and Cu for the ligands NTA and EDTA by DPP indicated that concentrations of complexes were not uniform throughout the cell (466). ASV analysis of very thin layers of solution eliminated the need for stirring and deaeration and used small samples (131).

A significant application of voltammetric methods is in the determination of stability constants for use in equilibrium models. These measurements can be made under controlled conditions that avoid interferences. The competitive interactions between trace metals and alkaline earths for ligands was studied (358). The stability constants of Pb, Cu, Cd, and Zn with hydroxyl and carbonate (47), and of $Zn(OH)_2$ (60) were determined. The complexation of Cd with EDTA in seawater was studied (308) and ASV was used to monitor Cu species in a flow bioassay system (313). In natural water samples, several workers have distinguished between free and labile ions, on one hand, and the total elemental forms by adjustment of pH (9,98,511,512).

The role of electroanalytical techniques for trace element speciation was discussed in general terms (96), and the speciation of Cu (349) and Zn (514) in seawater were studied. A polarographic method for distinguishing Fe(II) and Fe(III) in mine water was developed (476) as were conditions for the direct determination of CH_3Hg^+ in water (212). Se(IV) was determined at 4 ppb after ion-exchange separation (16). Organic As compounds were determined by DPP (45) and NO_3^- was determined by polarographic reduction at a Cu-Cd thin-film electrode (55). The organic complexation of Cu, Pb, and Cd in Great Lakes samples was reported (318). The organic complexing capacity of natural waters and effluents has been determined by titration with Cu(II) by using ASV as the analytical method (38,97,99,106,433,449). Co(III) was preferred as a titrant because it formed, with most ligands, stabile complexes that did not interfere in the subsequent determination of excess metal (200). An analytical procedure for trace levels of CN^- in natural waters and sewage was based on complexation with Cu and polarographic determination of the excess (27). Coulometric determinations of dissolved oxygen (262) and residual chlorine (315) have been applied to environmental samples.

Spectrometric Methods

Many ions can be determined quite specifically and sensitively by forming colored complexes with organic reagents. The color-forming reaction may disturb labile equilibria in the sample, however, and some care is needed to relate the measurement to the species in the sample. Errors in the diethyldithiocarbamate determination of Cu in natural waters were discussed (252). Colorimetric methods were listed in a review paper on the determination of anions in water (279). An automated colorimetric procedure for CN species (molecular HCN, free CN^-, and weak complexes) was developed (255). A colorimetric determination of $Cu(CN)_2$ was included in a complete analytical scheme for Cu speciation (463), and a spectrometric method has been published (396) for trace levels of Fe(II) in fresh and saline water. Ionization constants of NH_4^+, H_2S, HCN, HSCN, phenol, and several mercaptans were determined spectrophotometrically (487).

Laser Raman spectroscopy is a direct, but not highly sensitive, method for characterizing several ions in water. Detection limits of 25, 50, 50, and 100 ppm were found, respectively, for nitrate, phosphate, sulfate, and carbonate (24).

Biological Methods

The effects of inorganic species on biological systems were discussed in Section 4. Many of these effects, especially with enzymes, form the basis of very sensitive and specific analytical schemes, which have been reviewed (486). A bibliography on biological indicators of environmental quality gives additional applications (482). Immobilized nitrate reductase formed the basis of a sensitive continuous flow method for NO_3^- by providing very specific reduction of that species (421) and an automated continuous monitor for anti-cholinesterase agents showed a specific response to 10 ppm of Zn^{2+} (190).

Living organisms provide sensitive indications of pollutants but are generally less specific than enzymes. The role of bioassays has been reviewed (338). Bacteria were used to monitor a group of heavy metals at 2 to 3 ppm in industrial effluent (59) and the response of algae to copper was used to titrate organic chelators in seawater to 10^{-7} M (122,123).

Other Methods

The composition of particles and solid surfaces can be resolved by various electron and X-ray methods. High resolution X-ray spectrometry can distinguish valence states of some elements and was used to determine the ratio of S^{2-} to SO_4^{2-} in air particulates (187). Electron spectroscopy is the only technique that can give the oxidation state of surface elements at the ultra-trace level (144). Scanning electron microscopy in the X-ray imaging mode, combined with X-ray diffraction, showed that cadmium in contaminated marsh sediments was associated with calcium in mixed carbonate crystals (234). Photoelectron spectroscopy showed the distribution of cobalt species adsorbed on alumina (478).

Electron spin resonance identified Mn(II) species in water at 10^{-6} M and indicated that manganese was approximately in solubility equilibrium with $Mn(OH)_2$, but far from oxidation-reduction equilibrium (18).

Nitrite ion was determined by enthalpimetry of its reaction with sulfamic acid (205). The procedure required only a small sample (2 ml), had a detection limit about 70 ppb, and was free of interferences.

Kinetic and catalytic reactions are capable of great sensitivity and considerable specificity but seem to have been little applied to environmental analysis (65). Chemiluminescence methods can determine Cu(II), Co(II), Ni(II), Cr(III), Fe(II), or Mn(II) at 10^{-8} to 10^{-11} M (419). The technique found Cr(III) at 1 to 10 ppb in natural waters (420) and was used to determine total Fe (reduced to Fe(II) for analysis) in a variety of samples (418).

Isotope- and radio-tracer techniques are useful for following the distribution of an element among phases, or species because minute amounts of the tracer can be positively identifed by atomic mass or radiation. The technique has been recommended for studying the speciation of trace levels of Cd (379) and for following silt in rivers and reservoirs (405). The technique was used to check the efficiency of dialytic separations (30) and to show that Hg-humic complexes exchanged with fresh Hg(II) but not with other ions (469). There was negligible exchange between CH_3Hg^+ and Hg^{2+} in river water (272). Radio tracer methods have shown that marine systems slowly attain equilibrium with sediments (116) or with EDTA (175). Several workers have reported that radio-Zn was not distributed in biological species in the same manner as the stable isotope (43,78), possibly because the radio-isotope was not applied in the same chemical form as the natural element (299).

SEPARATION TECHNIQUES

Physical

Many speciation studies are restricted to a distinction between soluble or filtrable form, as determined by passage through a 0.45-μm membrane, versus total element (38,124,290,424). Some efforts have been made to define the size of very fine particles more closely--in the case of colloidal ferric hydroxide, by filtration through 0.2- and 0.1-μm membrane (423), or 0.05 μm membranes (87). Pores nominally 0.025 μm in diameter passed some forms of Pb less toxic than free Pb^{2+} (126). Molecular sieves (318) or gel permeation chromatography (221,318,377) have been used to fractionate organic complexes or ligands into molecular weight classes. Natural complexes of Co, Cu, Mn, and Zn did not pass through a dialysis membrane (30). Dialyzed inorganic solutions of Pb and Cd had the same total elemental composition as the original preparation, which was greater than the ionic form shown by DPP and also greater than the theoretical solubility limit (126).

Dialysis and centrifugation were used in another study of the hydrolytic speciation of Cd in dilute solutions (41).

The determination of unionized dissolved species in water, particularly gases, is needed because of their effects on aquatic life. Elemental S was determined by adsorption on XAD-2 resin, elution and concentration into cyclohexane, followed by gas chromatography (388). Two basic techniques have been used to remove molecular gases from solution for analysis. Sparging the sample with an inert gas is a direct method that works well for those gases having favorable distribution coefficients. When the molecular species is in equilibrium with ionic forms, it is important to remove only a small fraction of the dissolved gas to avoid displacing the equilibrium and this requirement limits the sensitivity. Accurate analytical procedures were developed for HCN (69) and for H_2S (71). Conflicting reports were given as to whether spargeable H_2S in sewage effluents was in equilibrium with sulfide ion, determined by the methylene blue colorimetric procedure (71,225).

The other major technique used to sample dissolved gases is diffusion across an air gap or through a semipermeable membrane. This procedure has been widely applied because it is rapid and removes only a small amount of gas for analysis. Oxygen, nitrogen, and carbon dioxide were sampled through a silastic membrane and determined by gas chromatography (264). The major application, however, is in gas-sensing electrodes in which the diffused gas establishes an ionic equilibrium in the absorbing electrolyte and is sensed by an appropriate ISE and reference electrode. The principles and construction of these devices have been described (169,397) and methods of calculating theoretical detection limits were given (23). Probes for CO_2 (432), NH_3 (351,481), and H_2S (225) were evaluated. The design of probes for SO_2, HCN, NO_2, and Cl_2 were given (397). The semipermeable membrane approach was used to sample HCN for colorimetric determination with a Technicon Autoanalyzer (154), and for sampling dissolved O_2 for coulometric determination (262).

Chemical

Chemical separations, even more than physical, entail the risk of disturbing the distribution of species unless the separation process is much faster than the competing transformations. Solvent extraction of organic complexes, such as the diethyldithiocarbamate complex of Cu (259), is a familiar technique for concentrating trace elements for subsequent photometric or AAS determination. Concentration techniques, including solvent extraction, have been thoroughly reviewed (153). Although these methods are intended primarily for total trace elements, some may be adaptable to ionic species. Stable natural complexes of Hg were separated by solvent extraction

(267). Extraction of sewage sludge with acetic acid gave a measure of available metals somewhat different than the total elemental analysis (44). Selective acid leaching of sediments gave an indication of adsorbed elements distinct from the substrate mineral (309). Extraction and leaching techniques were developed to partition the trace metals in sediments into characteristic groups (3,197).

Ion exchange chromatography permits the separation of ionic species or complexes (25,40,467). A fairly general procedure has been developed for the chromatography of the ions of strong electrolytes (443). Mercury species (25) and Ca and Mg (21) were separated and concentrated by ion exchange chromatography. Ion-exchangeable forms were distinguished from total dissolved metals (163) and anionic and cationic species were separately concentrated in the field on ion exchangers (430). Ion exchangers were also used as collecting agents to preconcentrate several ions without separating them (1,124,370,517). Ion exchange (186) and ultraviolet radiation (192) were used to decompose complex cyanides in the determination of total CN.

In principle, ion exchange membranes can be used to concentrate all ions of the same charge type in a sample by the same factor (51,53). Coupled with an ion-specific detector this technique should greatly extend capabilities for trace analysis and speciation. Applied to the determination of NO_3^-, the method was inconveniently slow, gave enrichment factors of less than 10, and was subject to several interferences (303). Commercial cation exchange membranes were unsatisfactory for the enrichment of Cu^{2+} in one trial (52), but gave more favorable results in another (112).

Differences in chemical reactivity can also be used to separate species. In an analytical scheme for the speciation of arsenic, varying pH of reduction and differing volatility of the products allowed six organic and inorganic forms to be determined in the same apparatus (62).

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